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MOBILITY OF ORGANIC COMPOUNDS FROM HAZARDOUS WASTES

by

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16. ABSTRACT

The objective of this research is to develop a second generation laboratory extraction test to model the mobility of organic and inorganic constituents from solid wastes co-disposed with municipal waste. This test should more accurately and reproducibly model leachate production, for selected organic as well as inorganic constituents, than the test procedure referred to as EP promulgated by EPA in 1980.

As a first approach the capabilities of five aqueous extraction procedures to remove organic compounds from 11 solid wastes were evaluated. The extraction procedures investigated were four batch extractions using (1) deionized distilled water adjusted to pH 5 with 0.5 N acetic acid, (2) deionized distilled water, (3) deionized distilled water with a sodium cation exchange resin (4) 0.5 M sodium citrate, and (5) an upward-flow column extraction using deionized distilled water. The major conclusions relative to the effectiveness of the extraction procedures to remove organic compounds were: (1) the column procedure extracted more organic material than any of the batch procedures, and (2) among the batch extraction procedures, deionized distilled water was the most aggressive medium.

The most noticeable differences between the column procedure utilized and the batch procedures were the elevated levels of moderately volatile and the nonpolar organic compounds found in the column extracts. Factors contributing to these results are: (1) the column procedure is a completely closed extraction permitting direct collection of volatile compounds, and (2) the column extracts were not filtered through membrane filters which are known to sorb appreciable quantities of nonpolar compounds.

Two extracting devices (magnetically stirred and rotary extractor) for conducting the EP were also compared. Extracts produced by the two extractors showed significantly different concentrations of As, Cd, Fe, Ni, and Zn, although neither method showed a consistent pattern.

The proposed reverse-phase High-Pressure Liquid Chromatography protocol to assess the bioaccumulation potential of solid waste extracts was found to produce only qualitative information because of nonuniformity of detector response. However, the test does provide a useful screening method for the detection of potentially bioaccumulative organic compounds.

In addressing a secondary research objective, comparison of two isolation techniques (i.e., resin adsorption technique using Amberlite XAD-2 resin and a solvent partition technique using methylene chloride) to isolate organic mutagens from aqueous solutions for testing in the Ames *Salmonella* mutagenicity assay was conducted. Although the assay results were not affected by the type of isolation technique used, the extraction efficiency of the resin technique was, in general, less dependent on the specific aqueous medium than was the solvent partition.

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ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectroscopy
BaP	Benzo(a)pyrene
DDE	2,2-bis-(p-chlorophenyl)-1, 1-dichloroethylene
DMSO	Dimethyl sulfoxide
DOC	Dissolved organic carbon
EP	Extraction Procedure (40 CFR 261.24)
EPA	U.S. Environmental Protection Agency
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HPLC	High-Pressure Liquid Chromatography
K-D	Kuderna-Danish
$MeCl_2$	Methylene chloride
NEIC	National Enforcement Investigations Center
NIPDWS	National Interim Primary Drinking Water Standards
ORNL	Oak Ridge National Laboratory
PTFE	Polytetrafluoroethylene
Pa	Pascals
RCRA	Resource Conservation and Recovery Act
rpm	Revolutions per minute
S	Siemens
TCO	Total Chromatographable Organic Compounds

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SECTION 1: INTRODUCTION

The disposal of municipal and industrial waste in landfills is a widely used waste management practice in the United States. It has become evident during the past few years that there has been serious environmental damage and possible adverse human health effects because of improper disposal of hazardous waste in landfills. Under the Resource Conservation and Recovery Act (RCRA) of 1976 (PL94-580), Congress directed the Environmental Protection Agency (EPA) to promulgate regulations to protect human health and the environment from improper management of solid wastes.

Under Section 3001 of RCRA, Identification and Listing of Hazardous Waste, EPA is charged with identifying which industrial wastes pose a hazard to human health or the environment if these wastes are improperly managed. On May 19, 1980 (EPA 1980b), EPA promulgated regulations that identified a number of properties of hazardous waste, which, if exhibited by a waste, would indicate that the waste requires controlled management. Under these regulations, toxicity of wastes is determined by the Extraction Procedure Toxicity Characteristic (40 CFR 261.24) which employs an Extraction Procedure (EP) to predict the degree to which toxic species might leach out of the waste and contaminate groundwater if the waste was disposed of in a nonsecure municipal landfill. The EP is a 24-h extraction procedure using 0.5 N acetic acid to adjust downward, if possible, the pH of the solid waste suspension to pH 5.0 (EPA 1980d). Additional information with regard to the development of the EP can be found in the EP Toxicity Characteristic Background Document (EPA 1980a).

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The EP results in an extract that is analyzed for the eight metals (As, Ba, Cd, Cr Pb, Hg, Se, and Ag), four pesticides (Endrin, Lindane, Methoxychlor, and Toxaphene), and two herbicides [2,4-D and 2,4,5-TP (Silvex)] for which National Interim Primary Drinking Water Standards (NIPDWS) (EPA 1979a) have been established. Hazardous waste definition threshold levels (Table 1.1) have been established for each of the species taking into account attenuative processes expected to occur during the movement of leachate through the underlying strata and groundwater aquifer.

The EP is considered to be a first-order approximation which primarily models the leaching action of the low molecular weight carboxylic acids generated in an actively decomposing municipal waste landfill. Acetic acid is added to distilled water to make up the extracting medium used in the EP. The acetic acid primarily affects the leaching of metals from an industrial waste. The higher molecular weight organics that are expected to be present in municipal landfill leachates, and thought to affect the leachability of nonpolar organics, are not currently modeled by the EP. This perceived limitation is the impetus behind the current research.

The primary objective of this research is to develop a second generation test for mobility that will more accurately and reproducibly model leachate production, for organic as well as inorganic constituents, in the previously described disposal environment. A second important objective of this research program is that the mobility test developed be compatible with subsequent biological testing.

TABLE 1.1. HAZARDOUS WASTE DEFINITION THRESHOLD LEVELS[a]

Contaminant	Maximum concentration (mg/L)
Arsenic	5.00
Barium	100.00
Cadmium	1.00
Chromium (IV)	5.00
Lead	5.00
Mercury	0.20
Selenium	1.00
Silver	5.00
Endrin (1,2,3,4,10,10-hexachloro-1, 7-epoxy-1,4,4a,5,6,7,8, 8a-octahydro-1, 4-endo, endo-5, 8-dimethano naphthalene)	0.020
Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer)	0.40
Methoxychlor (1,1,1-trichloro-2,2-bis [p-methoxyphenyl] ethane)	10.00
Toxaphene ($C_{10}H_{10}Cl_8$, technical chlorinated camphene, 67-69% chlorine)	0.50
2,4-D, (2,4-Dichlorophenoxyacetic acid)	10.00
2,4,5-TP; Silvex (2,4,5-Trichlorophenoxypropionic acid)	1.00

Source: 40 CFR 261.24

[a] Concentrations are 100 times the NIPDWS values.

Work toward these objectives has centered in four separate but related tasks as follows:

Task 1: An evaluation of aqueous extraction procedures to remove nonpolar organic compounds from solid wastes.

Task 2: A comparison of two sample preparation protocols for performing the Ames Test on solid waste extracts and wastewaters.

Task 3: An evaluation of the equivalence of a magnetically stirred extractor relative to an EPA-approved rotary extractor for conducting the EP.

Task 4: Evaluation of the proposed reverse-phase High Pressure Liquid Chromatography (HPLC) protocol for assessing the bioaccumulation potential of solid waste extracts.

SECTION 2: OBJECTIVES AND RATIONALE

2.1 Task 1: An Evaluation of Aqueous Extraction Procedures to Remove Nonpolar Organic Compounds from Solid Wastes

The primary objective of Task 1 was to assess the capabilities of five selected aqueous extraction procedures to remove organic compounds from 11 solid wastes known to contain significant quantities of organic compounds. Other objectives included (1) analyzing the solid waste extracts for selected inorganic constituents known to be present in the samples and (2) mutagenicity testing of the extracts. Mutagenicity testing was included to evaluate any differences in aggressiveness toward organic compounds among extraction procedures that might not be detected by GC/MS analyses; for example, the ability of an extraction procedure to extract high molecular weight mutagens from solid wastes.

A desirable, relevant extraction procedure should accurately and reliably model leachate production in the landfill situation, be relatively simple and economical to perform, and yield an extract that can be applied to biological assays. The five extraction procedures selected for this study were four batch extractions and an upward flow column extraction. The following extractants were used:

Batch 1: Deionized distilled water adjusted to pH 5 with 0.5 N acetic acid (EP).

Batch 2: Deionized distilled water.

Batch 3: Deionized distilled water with a sodium cation exchange resin.

Batch 4: 0.5 M sodium citrate buffer.

Column: Deionized distilled water.

A rationale for each procedure follows.

2.1.1 Batch 1: Environmental Protection Agency EP

The EP (EPA 1980b) is the test procedure promulgated by EPA under RCRA to determine if an unacceptably high level of groundwater contamination might result if an industrial waste is disposed of in a municipal landfill. The high ionic strength of the extracting solution and/or the method of membrane filtering the aqueous extract limits the recovery of organic compounds from a solid waste extract. The acetic acid used in the EP may also confound the interpretation of the phytotoxicity and aquatic toxicity assays (Epler et al. 1980).

2.1.2 Batch 2: Deionized Distilled Water Extractant

Deionized distilled water, because it introduces no extraneous interferences, is a reliable extractant to evaluate the toxicity of solid waste extracts in phytotoxicity and aquatic toxicity assays. In addition, distilled water at relatively high liquid:solid ratios tends to solubilize organics from solid wastes more efficiently than other aqueous extractants (McKown et al. 1980). For example, solutions containing citrate and acetate salts at high concentrations can enhance flocculation over dispersion.

2.1.3 Batch 3: Sodium-Resin Extractant

The solubility of organic compounds in groundwater is largely dependent on the "hardness" or "softness" of the water. Medium- and long-chain organic acids are solubilized when the "hard" calcium (or iron) is replaced by "soft" sodium. This is the basic principle in the extraction of fulvic and humic acids from soils by soil scientists (Schnitzer and Kahn 1972) (i.e., create a dispersed condition by substituting Na^+ for the dominant Ca^{+2} and Fe^{+3} ions). Conventionally, this is accomplished using 0.1 N NaOH. However, the high pH (11-12) does not represent environmental conditions. A sodium saturated chelating resin, added to a suspension displaces the dominant cations with sodium without significantly changing the pH of the suspension. The organic compounds are dispersed from the solid matrices, in effect solubilizing them in an aqueous environment.

2.1.4 Batch 4: Citrate Buffer Extractant

For certain solid wastes citrate buffer (0.5 M sodium citrate) was observed to be more aggressive than acetate or distilled water in leaching both organic compounds and metals; however, distilled water was the overall leaching medium of choice (McKown et al. 1980). The citrate butter was included because of an existing data base with citrate, the structural similiarity of citrate to other carboxylic acid esters present in municipal waste leachates, and the known capacity of citrate for complexing metals.

2.1.5 Column

An upward flow column extraction procedure was developed as a possible alternative to a batch extraction. Deionized distilled water is pumped upward through solid wastes packed in a glass column. Nonpolar organic compounds are collected directly on XAD-2 resin in series with the solid waste column; polar organic compounds remain in the eluent. Advantages of this system include:

(1) no time-consuming filtration step is needed,

(2) the extraction system is completely closed until the organic compounds are collected, thus loss of volatiles will be minimized,

(3) concentration of organic compounds is possible,

(4) column extraction of solid wastes more closely simulates the physical landfill leaching process, and

(5) column give dynamic data.

2.2 Task 2: A Comparison of Two Sample Preparation Protocols for Performing the Ames Test on Solid Waste Extracts and Wastewaters

The objective of this work was to compare two techniques for isolating organic mutagens from solid waste leachates and wastewaters for testing in the Ames *Salmonella* mutagenicity assay (Epler et al. 1980). The two recovery techniques compared were a resin adsorption technique using Amberlite XAD-2 resin and a solvent partition technique using methylene chloride. The XAD-2 resin technique has been used extensively at the Oak Ridge National Laboratory (ORNL) (Epler et al. 1980) and at EPA's Health Effects Research Laboratory at Research Triangle Park, North Carolina, while the solvent partition scheme is the one recently developed by the National Enforcement Investigations Center (NEIC), Denver, Colorado (EPA 1980c). The objective of this task was to determine if significant differences were obtained in the Ames *Salmonella* mutagenicity assay when using either of the two preparation protocols.

2.3 Task 3: Assessment of a Magnetically Stirred Extractor Relative to an EPA-Approved Rotary Extractor for Conducting the Extraction Procedure (EP)

The objective of this task was to compare a magnetically stirred extractor to an EPA-approved rotary extractor for conducting the EP. An acceptable extractor to conduct the EP was described in "Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods" (EPA 1980) as "...one which will prevent stratification of a waste sample and extraction fluid and will insure that all sample surfaces continuously contact well mixed extraction fluid. Among the acceptable extractors are: (1) stirrers and (2) tumblers. Stirrers consist of a container in which the waste/extraction fluid mixture is agitated by spinning blades. Rotators agitate by turning a sample container end over end through a 360° revolution."

The magnetically stirred extractor consists of a glass vessel and polytetrafluoroethylene (PTFE)-coated stirring bar in concert with a commercially available magnetic stirrer readily available in most laboratories. This design appeared to satisfy all of the above requirements. The magnetically stirred extractor offers certain advantages in that, in contrast to the rotary extractor design, the pH of the suspension can be automatically adjusted. In addition, the glass vessel and PTFE-coated magnetic stir bar eliminates the possibility of contamination by the spinning stainless steel blades used in several of the EP extractor designs.

2.4 Task 4: Evaluation of the Proposed Reverse-Phase High-Pressure Liquid Chromatography (HPLC) Protocol for Assessing Bioaccumulation Potential of Solid Waste Extracts

The objective of this task was to evaluate the analytical constraints and interpretations associated with using the proposed reverse-phase High-Pressure Liquid Chromatography (HPLC) protocol (EPA 1978a and EPA 1978b) to assess the bioaccumulation potential of solid waste extracts. It has been shown that there is a relationship between octanol/water partition coefficients and bioaccumulation potential (i.e., compounds with high octanol/water partition coefficients have the potential to biologically accumulate) and between octanol/water partition coefficients and the log of reverse-phase HPLC retention times. Plotting the log of reverse-phase HPLC retention times of solid waste extracts (from Task 1) against the log of the octanol/water partition coefficients of known compounds should provide a method to estimate the potential for the components in the solid waste extracts to accumulate in biological tissues.

SECTION 3: EXPERIMENTAL

3.1 Description of Solid Wastes

Eleven solid wastes from a variety of industries were obtained for use in Task 1. The particular wastes were selected because they were thought to contain toxic organic compounds. Table 3.1 contains a short description of the wastes used for Task 1 and other studies. Wastes 1 through 6 were taken from actual landfills. Corresponding landfill leachates were also sampled in a related study comparing the solid waste EP extracts with the landfill leachates (Brown et al. 1981). Waste samples 7 through 11 are oily in nature and were selected based on a prediction that this oily component would challenge the extraction procedures. Wastes 7 and 8 changed physically (i.e., the oily components separated from the remainder of the sample) during the course of the study. For this reason, not all extractions were performed on these wastes.

Two additional waste samples (12 and 13) were selected for use in Task 3. Both were selected because they contained leachable inorganic elements and were expected to pose stirring problems with the magnetic stirrer. An additional waste (14) was utilized for the supplementary filtration study in Task 1.

General sample information, such as water content and general physical description of wastes 1 to 14, is presented in Table 3.2. Water content was determined by gas chromatography as described by Shultz and Spears (1966).

TABLE 3.1. DESCRIPTION OF WASTES

Waste	Waste description
Used for Task 1:	
1	Sludge from the production of feed additives and veterinary pharmaceuticals
2	Sludge from the treatment of a municipal sewage, a cannery waste, and tannery wastes
3	Paper mill sludge
4	Municipal refuse and local industrial waste (plastic laminate and electronics waste)
5	Paper mill, paper trimmings, and related wastes
6	Municipal wastewater treatment sludge mixed with local industrial waste (plastic and textile mill)
7	Wastewater treatment sludge from a metal processing plant
8	Untreated washing sludge from a metal bearing factory
9	Wastewater treatment sludge from a coal conversion plant
10	Filter cake from a coal conversion biological treatment plant
11	Centrifuged heavy oil residuals from a coal conversion wastewater treatment plant
Used for Task 3:	
12	Ash from a coal conversion facility
13	Fly ash from a coal-fired power plant
Used for Filtration Study:	
14	Vacuum bottoms from a coal conversion facility

TABLE 3.2. WASTE CHARACTERISTICS

Waste	Water content[a] (weight %)	Waste characteristics
1	33	Yellowish green, dark; pasty texture
2	55	Dark grey sludge containing hair, hide, etc.; strong odor
3	56	Dark brown, nearly opaque, sandy sludge; noticeable aroma
4	77	Sawdust-like texture; yellow-orange
5	62	Like flaked cardboard; dark purple
6	60	Very dark gray, clay-like consistency; strong odor
7	nd[b]	Watery, dark brown; slightly aromatic
8	nd	Dark brown, thick, oily liquid; oily odor
9	60	Black, oily sludge; rubbery consistency
10	41	Charcoal gray, sandy, and granular; irritating odor
11	59	Black, oily sludge; irritating odor
12	nd	Hard granular solid containing Cd, Fe, and Ni.
13	nd	Fine solid, high in magnetite, contains As, Cd, and Zn
14	<1.0	Dark-colored dry powdery solid.

[a] As determined by the method of Shultz and Spears (1966).

[b] nd = not determined.

Many of the wastes, because they contained significant quantities of organic compounds, had the potential to change during the course of the study due to biological activity. To slow down such changes, each waste was thoroughly mixed and subsampled into 200- to 500-g quantities. The subsamples were placed in glass containers and frozen at -15°C. Samples were thawed in the refrigerator (4°C) the day prior to extraction.

3.2 Methods

3.2.1 Isolation of Organic Compounds in Solid Wastes

Identification of the major organic constituents from the wastes was carried out using the following two procedures:

(1) Twenty-four-hour Soxhlet extraction with methylene chloride, followed by volume reduction in a Kuderna-Danish (K-D) evaporator (EPA 1980d).

(2) A three-step sequential extraction procedure developed at ORNL (Fig. 3.1; Maskarinec and Harvey 1982).

The isolates from procedures (1) and (2) were compared by gravimetry as well as by gas chromatography.

Volatile organic compounds were determined in selected wastes using the apparatus shown in Fig. 3.2. This apparatus is a simple modification of the existing purge and trap devices that allows the purging of solid materials without dissolution in water (Brazell and Maskarinec 1981).

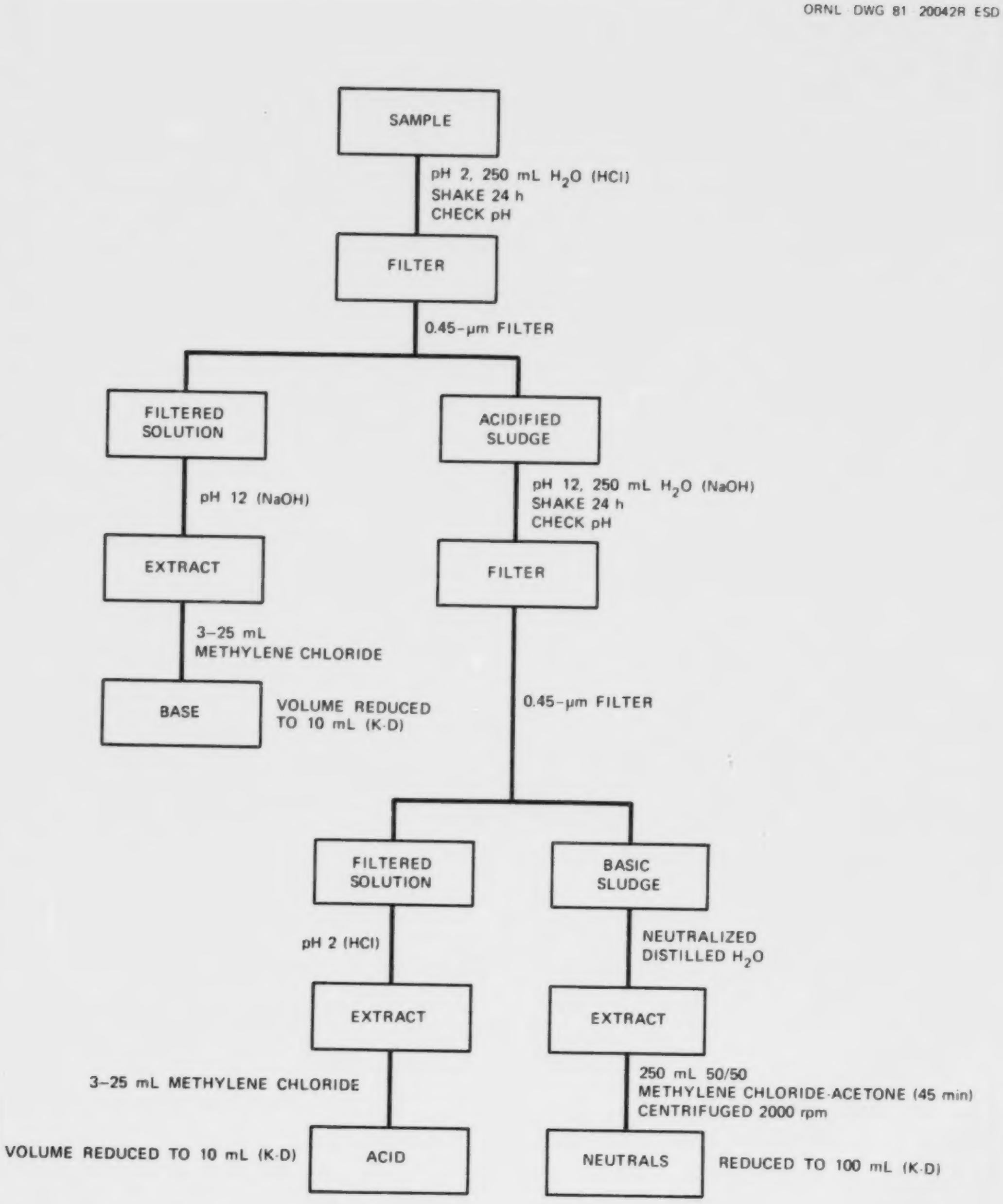
ORNL DWG 81 20042R ESD
SAMPLE
pH 2, 250 mL H_2O (HCl)
SHAKE 24 h
CHECK pH
FILTER
0.45-μm FILTER
FILTERED SOLUTION
ACIDIFIED SLUDGE
pH 12 (NaOH)
pH 12, 250 mL H_2O (NaOH)
SHAKE 24 h
CHECK pH
EXTRACT
FILTER
3–25 mL
METHYLENE CHLORIDE
BASE
VOLUME REDUCED
TO 10 mL (K-D)
0.45-μm FILTER
FILTERED SOLUTION
BASIC SLUDGE
pH 2 (HCl)
NEUTRALIZED
DISTILLED H_2O
EXTRACT
EXTRACT
3–25 mL METHYLENE CHLORIDE
250 mL 50/50
METHYLENE CHLORIDE-ACETONE (45 min)
CENTRIFUGED 2000 rpm
VOLUME REDUCED TO 10 mL (K-D)
ACID
NEUTRALS
REDUCED TO 100 mL (K-D)

Fig. 3.1. Scheme for proximate analysis of solid wastes and sludges by sequential extraction.

ORNL-DWG 81-6937

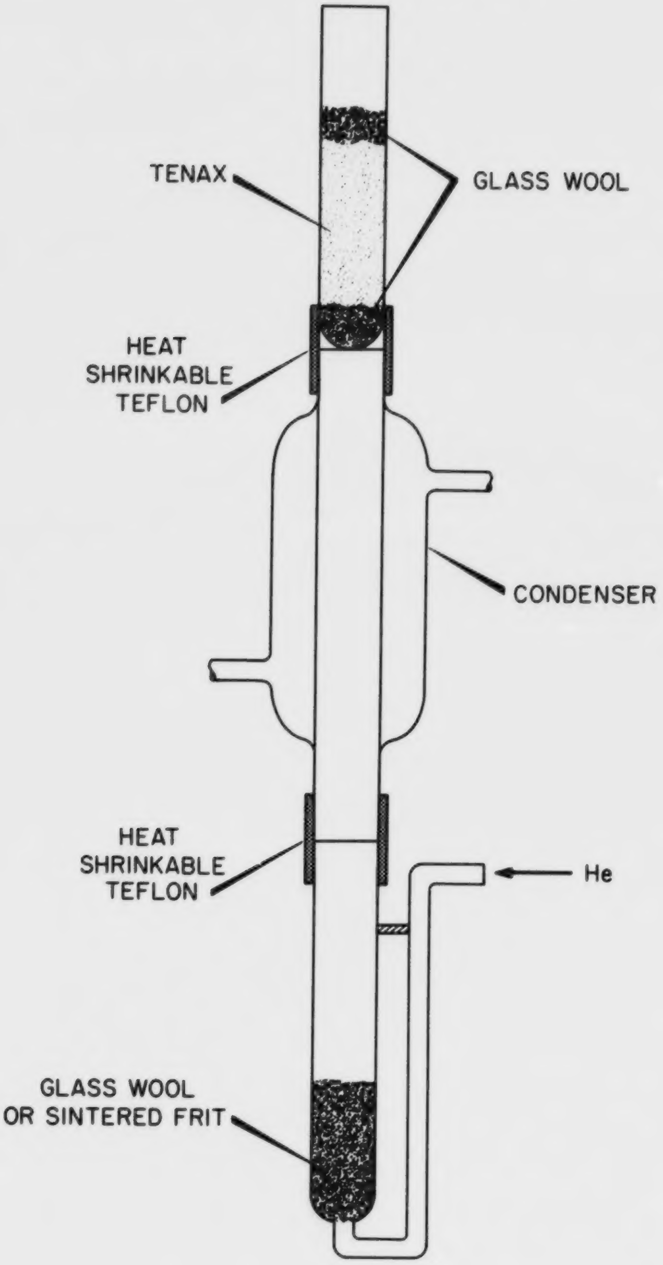
TENAX
GLASS WOOL
HEAT SHRINKABLE TEFLON
CONDENSER
HEAT SHRINKABLE TEFLON
He
GLASS WOOL OR SINTERED FRIT

Fig. 3.2. Apparatus used for isolation of volatiles.

3.2.2 Solid Waste Extraction Procedures

In this study, five aqueous extraction procedures were evaluated and compared for ability to extract both inorganic and organic components. Table 3.3 contains a listing of the five extraction procedures, with a compilation of variable leaching factors. Table 3.4 contains a listing of equipment and materials used for the five extraction methods. All extractions were carried out to a liquid to solid ratio of 20:1.

The EP was performed according to the current regulatory protocol (EPA 1980d), using 185 g of wastes. Wastes were placed in borosilicate glass vessels with 2.96 L of deionized distilled water (ASTM, Type I Reagent Water). The vessel was fabricated at ORNL from 6.35-mm-thick, 152.4-cm-i.d. (inside diameter) flanged glass pipe that could hold up to 4.0 L of solution. A fitted vessel cover was constructed of plexiglass, with holes cut in it to admit a pH electrode and tubing (for adding acid). The solid waste suspensions were agitated for 24 h using a magnetic stirrer and 76.2-mm PTFE-coated stir bar. During the 24-h extraction, the pH of the solution was automatically adjusted to pH 5 using 0.5 N acetic acid. A maximum amount of 4 mL of acid per gram of waste extracted is specified in the protocol. If less than the maximum amount of acid was used during extraction, the extract was diluted with deionized distilled water to a final 1:20 solid:liquid ratio prior to filtering.

The water extractions were performed as in the EP with the exception that 3.7 L of deionized distilled water (ASTM, Type I Reagent Water) were initially added to 185 g of waste (1:20 solid:liquid ratio). There was no pH adjustment during extraction.

TABLE 3.3. EXTRACTION PROCEDURES: IDENTIFICATION OF VARIABLE LEACHING FACTORS

	Variable factors[a]			
Extraction	Initial leaching medium	Mode of extraction	pH adjustment	Treatment of leachate solution for extract analysis
1. Batch 1: EP	Deionized distilled water[b]	Batch: magnetically stirred	Adjust to pH 5 with 0.5 N acetic acid - maximum limit of 2-meq/g sample	Pressure-filtered through 0.4-μm Nuclepore filter
2. Batch 2: Water	Deionized distilled water[b]	Batch: magnetically stirred	None	Pressure-filtered through 0.4-μm Nuclepore filter
3. Batch 3: Na-resin	Deionized distilled water[b] with 1-g calculated dry wt Chelex 100/10-g sample	Batch: magnetically stirred	Adjust to pH 7 with 0.1 N HCl	Pressure-filtered through 0.4-μm Nuclepore filter
4. Batch 4: Citrate buffer	0.5 M citrate buffer	Batch: rotary extractor	None	Pressure-filtered through 0.4-μm Nuclepore filter
5. Up-flow column	Deionized distilled water[b]	Column: upward flow	None	Leachate from column directly passed through XAD-2 resin

[a] Factors such as particle size (<9.5 mm), extraction at room temperature, extraction time (24 h for batch extractions or until an effect 1:20 solid:liquid ratio contact is reached for column extraction), one extraction on each waste, and effective 1:20 solid:liquid ratio remained constant.

[b] ASTM, Type I Reagent Water.

TABLE 3.4. EQUIPMENT AND MATERIALS USED FOR THE EXTRACTION PROCEDURES

Item		Manufacture or supplier[a]	Catalog Number
Magnetic stirrer		Cole-Parmer	C-4817-00
Teflon stir bar		Cole-Parmer	C-4612-30
pH controller		Chemtrix	45AR
pH electrode		Leeds & Northrop	117493
Filtration apparatus		Millipore Corp.	YT30-142-HW
Filters	0.40-μm pore size	Nuclepore Corp.	112207
	0.8-μm pore size	Nuclepore Corp.	112209
	3.0-μm pore size	Nuclepore Corp.	112212
Pre-filters	P40	Nuclepore Corp.	211703
	P80	Nuclepore Corp.	211705
	P100	Nuclepore Corp.	211707
	P300	Nuclepore Corp.	211708
Drain disc		Nuclepore Corp.	231700
Rotary extractor		Associated Design & Mfg. Co.	3740-6-BRE
Glass column		Glenco Scientific	3400-D-25X45
Pump		Lab. Data Control, Div. of Milton Roy	2396-57
Sea sand, sieve distribution: 20 to 35 mesh - 8%; 36 to 50 mesh - 51%; 51 to 60 mesh - 18%; 61 to 70 mesh - 7%; 71 to 100 mesh - 13%; and 100 mesh - 3%.		Fisher Scientific	S-25

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[a] Use of a specific manufacturer or supplier does not imply the endorsement by either Oak Ridge National Laboratory or the U.S. Environmental Protection Agency.

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The sodium resin displacement extraction was also performed in the same manner as the EP. Initially, 2.96 L of deionized distilled water (ASTM, Type I Reagent Water) and 92.5 g of Chelex 100 resin (Bio Rad Laboratories, 100-200 mesh, sodium form) was added to 185 g of sample. The suspension was adjusted to pH 7 using 0.1 N HCl. This pH adjustment was performed to make the final extract more suitable for phytotoxicity and aquatic toxicity bioassays. The final extract was also diluted to a final 1:20 solid:liquid ratio prior to filtration.

The citrate buffer extractions were performed according to the procedure of McKown et al. (1980). This procedure specified the use of a rotary extractor which tumbles solid waste suspensions end-over-end in closed glass containers. A 75-g sample was placed in the glass container with 1.5 L of 0.5 M citrate buffer. The tumbling rate was 29 rpm.

Following a 24-h extraction using the above-mentioned batch procedures, the component solid and liquid phases were separated by pressure filtration at 5.2×10^5 Pa (75 psi), and the final extract was passed through a 0.4-μm polycarbonate filter (Nuclepore). In most cases, a series of filters having decreasing pore sizes was needed in the filter stack. Even though the filter stack was changed, as deemed necessary, some suspensions took considerable time to filter (as much as 1-2 days).

For column extraction, 100 g of solid waste was thoroughly mixed with 100 g of acid-washed sea sand to increase the hydraulic conductivity of the samples. A glass column 2.5 cm i.d. and 45 cm long (with plungers on each end adjustable to the varying bulk density of the samples) was packed with the solid waste/sand mixture. A 2.5-cm layer of sand was placed on each end of the column. Figure 3.3 schematically shows the column extraction apparatus. For this study, deionized distilled water (ASTM, Type I Reagent Water, passed through XAD-2 resin to remove trace organic material) was pumped upward through the solid waste/sand mixture until 2 L had passed through the sample. A relief valve, set at 5.1×10^5 Pa (60 psi) was used to avoid unsafe stresses on the glass column. The column effluent was passed through a 10-μm pore size PTFE cloth (located on the top plunger) and then directly through an XAD-2 resin cartridge (16.8 mL) for collection of organic compounds.

The pH, amount of acid added during extraction (for extractions requiring pH adjustment), and electrical conductivity were recorded on the 11 samples during each of the five extraction procedures (Tables 3.5-3.9). Solution pH is an important factor when considering dissolution/precipitation and sorption reactions that may be occurring during extraction. These data are provided as accessory information on the wastes (e.g., the solid waste's buffering capacity).

Following extraction, all samples were stored and preserved according to the desired analysis as follows:

(1) organic compounds - stored in glass containers and refrigerated at 4°C,

(2) Hg analysis - placed in glass volumetric flask with dichromate/nitric acid preservative,

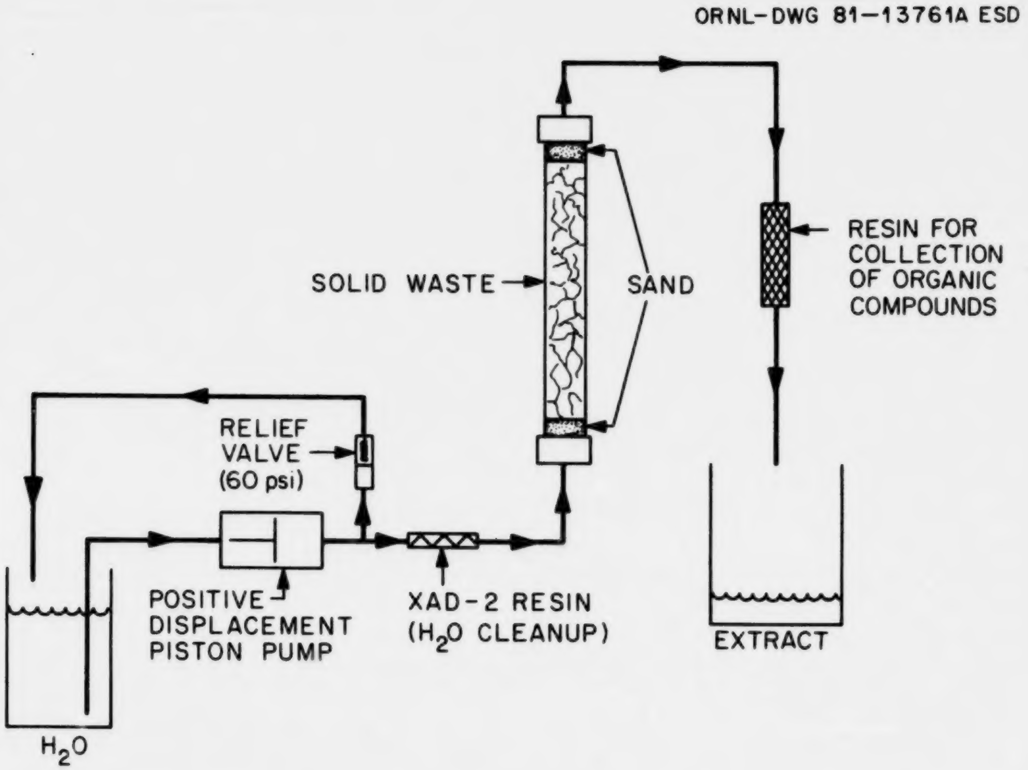
ORNL-DWG 81-13761A ESD
SOLID WASTE
SAND
RESIN FOR COLLECTION OF ORGANIC COMPOUNDS
RELIEF VALVE (60 psi)
POSITIVE DISPLACEMENT PISTON PUMP
XAD-2 RESIN (H_2O CLEANUP)
EXTRACT
H_2O

Fig. 3.3. Column extraction apparatus.

TABLE 3.5. BATCH 1: EP EXTRACTION DATA

Waste	Replication Number	Initial solution pH (1:16 solid:solution ratio)	Acetic acid initially added (meq/g sample)	Total acetic acid added (meq/g sample)	Final EP extract		
					pH	Electrical conductivity (μS/cm)	Color
1		8.7	2.0[a]	2.0[a]	6.1	2750	Transparent, dark yellow
2	1	7.5	0.65	0.79	5.0	2440	Translucent, colorless
	2	7.1	0.54	0.68	5.0	2150	
3		7.1	2.0[a]	2.0[a]	6.0	3300	Transparent, yellow-grey
4		7.5	0.03	0.07	4.8	498	Transparent, pale yellow
5		7.4	0.04	0.11	4.7	150	Transparent, colorless
6		5.3	0.02	0.12	5.0	100	Transparent, yellow
7[b]							
8		6.5	0.36	0.38	5.1	2750	Transparent, green tint
9		7.0	0.23	0.38	5.1	418	Transparent, colorless
10	1	12.0	2.0[a]	2.0[a]	12.0	6575	Transparent, pale yellow
	2	12.0	2.0[a]	2.0[a]	11.9	7600	Transparent, pale yellow
	3	11.6	2.0[a]	2.0[a]	12.2	7550	Transparent, pale yellow
11		5.6	0.02	0.03	5.2	85	Transparent, pale yellow tint

[a] Maximum amount allowed (4 mL acid/g sample).

[b] Not extracted.

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TABLE 3.6. BATCH 2: WATER EXTRACTION DATA

Waste	Initial solution pH	Final solution pH (before filtering)	Final filtered extract pH	Final filtered extract Electrical conductivity (μS/cm)	Final filtered extract Color
1	8.8	8.8	8.8	2000	Transparent, yellow-orange
2	8.0	7.8	8.0	1620	Transparent, yellow-green
3	6.6	7.1	7.0	820	Opaque, tan
4	7.8	7.0	6.8	410	Transparent, pink
5	6.8	7.0	7.4	252	Transparent, pink
6	6.3	6.4	6.7	1500	Opaque, yellow-brown
7	6.1	6.6	6.0	121	Transparent, colorless
8	8.1	8.8	8.2	150	Transparent, pale-gold
9	7.5	6.3	6.5	307	Transparent, colorless
10	11.7	12.4	12.0	6620	Transparent, gold
11	5.9	5.8	6.0	69	Transparent, pale yellow

TABLE 3.7. BATCH 3: Na-RESIN EXTRACTION DATA

Waste	Initial solution pH	Solution pH after resin addition	Amount of HCl added to adjust solution to pH 7 (meq/g sample)	Final pH (before filtering)	Final filtered extract		
					pH	Electrical conductivity (µS/cm)	Color
1	8.3	7.0	0.0	6.8	7.0	2700	Transparent, yellow-orange
2	8.2	7.8	0.096	7.1	7.4	2125	Transparent, colorless
3	6.9	7.5	0.072	7.1	7.5	1160	Translucent, gold
4	7.4	7.9	0.014	7.1	7.2	428	Transparent, apple cider colored
5	7.6	8.1	0.028	7.2	7.7	425	Transparent, pale orange
6	5.3	5.9	0.0	5.9	6.4	782	Translucent, pale yellow
7	6.1	7.8	0.027	7.0	7.2	460	Transparent, tan
8	7.3	8.3	0.032	7.1	7.4	345	Transparent, tan
9	7.5	7.8	0.009	6.5	7.2	450	Transparent, black tint
10	11.4	11.5	0.4	12.4	12.1	7750	Transparent, pale gold
11	5.8	6.3	0.028	7.0	7.2	450	Transparent, pale yellow
Blank	4.8	9.5	0.022	7.15	7.0	165	Transparent, colorless

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TABLE 3.8. BATCH 4: CITRATE BUFFER EXTRACTION DATA

Waste	Final pH filtered extract	Electrical conductivity (μS/cm)	Color
1	4.5	7555	Transparent, yellow
2	7.2	7600	Transparent, pale yellow
3	8.0	5300	Opaque, dark brown/black
4	5.1	5200	Transparent, yellow
5	5.4	5800	Transparent, pale orange
6	5.4	6100	Transparent, yellow
7[a]			
8	5.0	5800	Transparent, pale gold
9	5.1	5850	Transparent, pale yellow
10	12.3	10800	Transparent, amber
11	5.3	nd[b]	Transparent, apple cider colored

[a] Not extracted.

[b] nd = not determined.

TABLE 3.9. MEASUREMENTS OF pH AND ELECTRICAL CONDUCTIVITY IN COLUMN EXTRACTS AFTER PASSING THROUGH XAD-2 RESIN

Waste	Replication	pH	Electricity conductivity (μS/cm)
1		7.9	1999
2	1	7.6	1500
	2	7.2	910
3		6.9	1175
4	1	7.8	741
	2	6.4	560
5		6.8	388
6		6.5	1025
9		7.4	550
10	1	12.1	6150
	2	10.8	4900
	3	10.5	2460
11		5.2	20

(3) all other metals - placed in plastic containers, preserved with Ultrex nitric acid (solution pH < 2) and refrigerated at 4°C (EPA 1979b), and

(4) volatile organic compounds - stored in 25-mL glass bottles with no head space at 4°C.

3.2.3 Filtration Study (Supplemental to Task 1)

A filtration study was conducted to determine if decreased levels of organic compounds measured in the batch extract resulted from sorption of nonpolar organic compounds during filtration through a 0.4-µm nominal pore size membrane filters. As described earlier, the column extracts were passed through a 10-µm pore size PTFE cloth at the top of the column before the collection of organics on an XAD-2 resin. The two objectives of the filtration study were to determine if the XAD-2 resin had collected entrained organic particulates (less than 10 µm) from the column that might be filtered out if filtered through a 0.4-µm membrane filter and to examine the recovery of organic compounds in four solid/liquid phase separation treatments. The four separation treatments were:

(1) filtration through a precombusted glass fiber filter (Whatman GF/F, approximately 0.7-µm pore size),

(2) filtration through a Nuclepore filter (polycarbonate, 0.4-µm pore size),

(3) filtration through a Millipore filter (type HA - mixed esters of cellulose, 0.4-µm pore size), and

(4) centrifugation (in 250-mL glass bottles, 400 times gravity for 1 h).

Using 100-g samples of waste 14, four extractions were conducted as follows with deionized distilled water as the extractant:

(1) column extraction performed as described in Section 3.2.2 (i.e., extract from the column passed directly through a 16.8-mL XAD-2 resin cartridge),

(2) column extraction performed like (1) above, except a glass fiber filter was placed in line prior to the effluent passing through the XAD-2 resin cartridge,

(3) column extraction performed like (1) above with the effluent subjected to the above listed four solid/liquid phase separation treatments, and

(4) batch extraction was performed on the rotary extractor; the suspension then subjected to the four solid/liquid phase separation treatments.

In addition, 4 L of a standard solution were prepared with known organic compounds at concentrations of 10 ppm. Two liters of this solution were then immediately subjected to the same four separation treatments. The remaining 2 L of this standard solution from above were agitated for 24 h with the rotary extractor. The solution was then subjected to the four solid/liquid phase separation treatments.

3.2.4 Isolation of Organics for Mutagenicity Testing - Task 2

Two recovery techniques (Fig. 3.4), a resin adsorption technique (Epler et al. 1980) using Amberlite XAD-2 resin (resin cartridges as used in Task 1) and a solvent partition technique using methylene chloride (EPA 1980c), were compared for the isolation of organic mutagens from aqueous solutions. Two known mutagens were used as

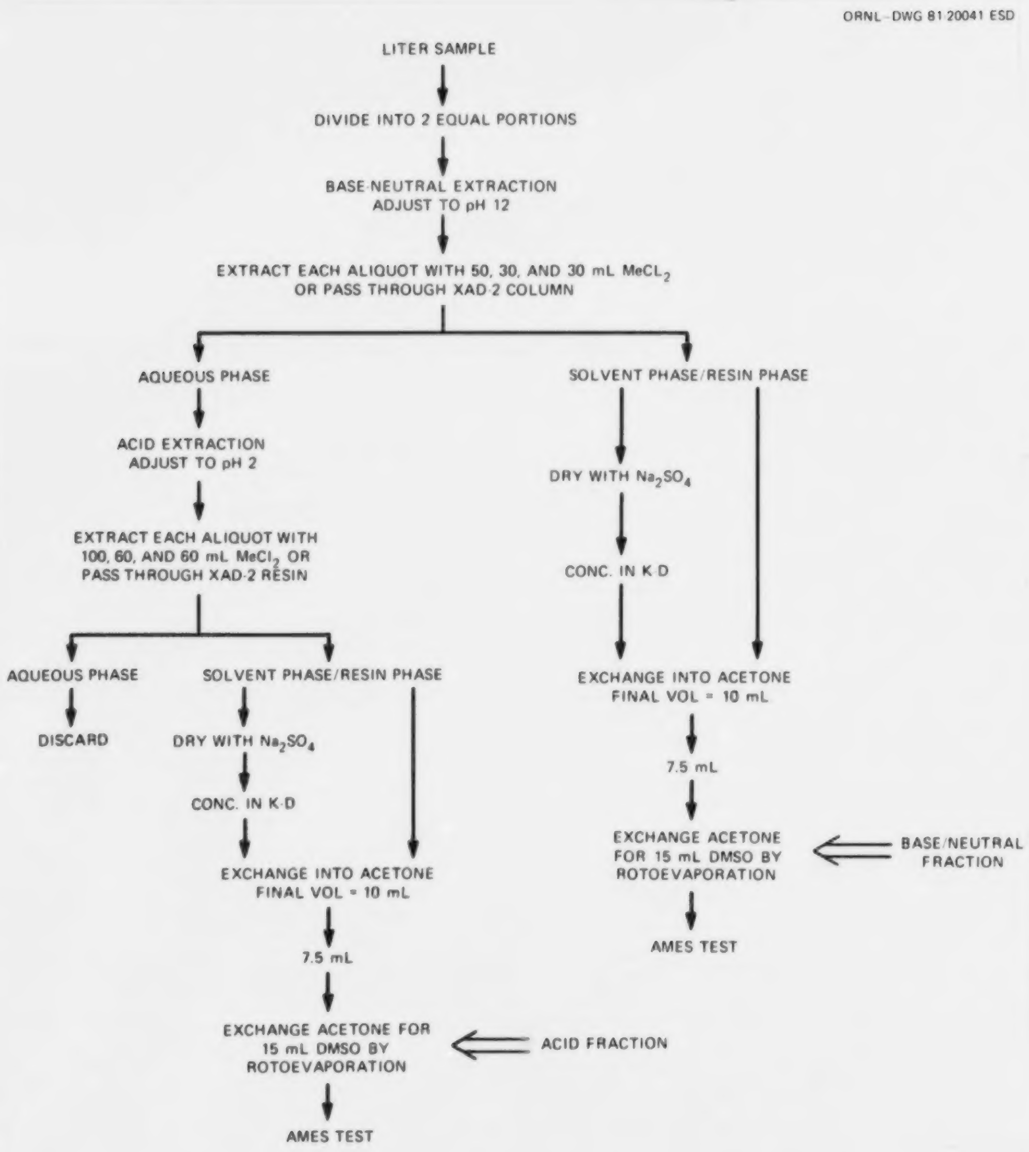
ORNL-DWG 81-20041 ESD
LITER SAMPLE
DIVIDE INTO 2 EQUAL PORTIONS
BASE-NEUTRAL EXTRACTION
ADJUST TO pH 12
EXTRACT EACH ALIQUOT WITH 50, 30, AND 30 mL $MeCL_2$
OR PASS THROUGH XAD-2 COLUMN
AQUEOUS PHASE
SOLVENT PHASE/RESIN PHASE
ACID EXTRACTION
ADJUST TO pH 2
DRY WITH Na_2SO_4
EXTRACT EACH ALIQUOT WITH
100, 60, AND 60 mL $MeCl_2$ OR
PASS THROUGH XAD-2 RESIN
CONC. IN K-D
AQUEOUS PHASE
SOLVENT PHASE/RESIN PHASE
EXCHANGE INTO ACETONE
FINAL VOL = 10 mL
DISCARD
DRY WITH Na_2SO_4
7.5 mL
CONC. IN K-D
EXCHANGE ACETONE
FOR 15 mL DMSO BY
ROTOEVAPORATION
BASE/NEUTRAL
FRACTION
EXCHANGE INTO ACETONE
FINAL VOL = 10 mL
AMES TEST
7.5 mL
EXCHANGE ACETONE FOR
15 mL DMSO BY
ROTOEVAPORATION
ACID FRACTION
AMES TEST

Fig. 3.4. Extraction procedures for environmental water samples.

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markers, representing the base (9-amino acridine) and neutral [benzo(a)pyrene] chemical classes. The mutagens were purified to the highest possible level and dissolved in dimethysulfoxide (1 mg/mL). The aqueous media included:

(1) distilled water,
(2) a solid waste EP extract (waste 10),
(3) a "real-world" landfill leachate (from waste 3), and
(4) an industrial wastewater.

All aqueous media and all extraction blanks were tested for indigenous mutagenic effects. These four aqueous media were chosen to give large variety, both in terms of physical characteristics and possible chemical interferences.

Mutagens were added to each aqueous medium in an amount sufficient to give an unambiguous response in the Ames test (1 mg/L of water). A sufficient volume (4 L) of each aqueous medium was used for both recovery techniques (eight 500-mL aliquots: 2 replicates x 2 treatments x 2 mutagens). Since the required level of BaP was in exess of its solubility, the mutagen was added directly to the aqueous medium contained in a separatory funnel. The funnel was shaken once, the pH was adjusted, and the extraction was begun immediately. The separatory funnel/resin system was not disconnected until the extraction was completed. Thus, any components precipitated out by pH adjustment or sorbed onto the funnel were extracted with the organic solvent. The same procedure was used for the 9-amino acridine. An analysis of variance was performed to determine significant differences between the recovery techniques. The recovery of benzo(a)pyrene (containing tracer levels of ^{14}C-labeled benzo(a)pyrene below mutagenic radio-activation threshold values) was measured by liquid scintillation counting as well as by reverse-phase HPLC. The 9-amino-acridine recovery was measured by fluorescence spectrometry at several dilutions using the standard addition method.

3.2.5 Assessment of Extracting Devices for Conducting the EP - Task 3

Two extracting devices (magnetically stirred and rotary extractor) were compared for Task 3. The magnetically stirred extractor at both a high and low mixing rate and the rotary extractor at 29 rpm were examined for conducting the EP (EPA 1980b and EPA 1980d). The low mixing rate utilized in the magnetic stirrer was the lowest speed that could be achieved while still keeping solids suspended, and the high mixing rate utilized was the highest speed at which the stir bar could be controlled.

A factorially designed experiment was conducted using the three mixing rates, two wastes (Nos. 12 and 13), four extraction replicates, and three analytical determinations of each extract. Two statistical treatments of the data were performed (SAS Institute, Inc., 1979): variance component analysis and the Duncan's multiple range test.

Stirrer-speed determinations using the magnetic stirrer were made using a low-frequency tachometer designed at ORNL. A description of this device follows. A photon coupled interruptor module was installed in the magnetic stirrer, beneath the plate. A disc with 64 slits was attached to the magnet shaft in the stirrer. As the magnet rotates, the disc over an optical sensor (utilizing infrared) generates 64 pulses for each revolution. The pulses are fed into a three-channel low-frequency tachometer where, using integrated circuitry, each of the 64 pulses is converted to a d.c. voltage (equal to 1 rpm). The output is then transferred to a strip chart recorder.

3.3 Methods of Analysis

3.3.1 Inorganic Analyses

All extracts analyzed for inorganic constituents were treated according to standard methods (EPA 1979b) and were directly analyzed for metals by flameless graphite furnace atomic absorption spectroscopy (AAS) with the following exceptions:

(1) extracts for Hg determination were preserved by addition to a nitric acid/dichromate solution and worked up for cold vapor flameless AAS (Feldman 1974),

(2) Se was chelated with 5-nitro-o-phenylene diamine and extracted with toluene before analysis (Talmi and Andren 1974), and

(3) As was determined by an arsine accumulation-helium glow detector procedure (Feldman 1979).

Samples were analyzed by the method of standard addition (EPA 1979b).

Because the primary focus of this study was organic content of various solid waste extracts, only selected elements believed to be in high concentrations were examined in the batch-type extractions. The elements were generally limited to those found in the NIPDWS (EPA 1979a) because they are used to identify toxic constituents in EP extracts. However, Fe, Ni, SO_4^{-2}, and Zn were measured in selected extracts as well.

3.3.2 Organic Analyses

The organic analysis of the various aqueous batch extracts was carried out by first adjusting the aqueous extract to pH 6.8 using phosphate buffer and to a conductivity of 20 mS/cm using sodium chloride. The adjusted extract (500 mL) was then passed through a cartridge containing 4.2 mL XAD-2 resin (XAD-2 resin was obtained in pre-cleaned, pre-filled form from Isolab, Inc., Akron, Ohio). Previous work (Epler et al. 1980) had shown that these conditions were effective for the extraction of nonpolar organic compounds, of primary interest in this work. This extraction technique effectively excludes the acetic acid used in the EP and the citric acid used as an alternative test extractant. In addition, the XAD technique avoids the problems often encountered in the solvent partition techniques where high concentrations of organic acids (such as acetic and citric acids) tend to produce stabel emulsions, complicating the separation of the aqueous and nonaqueous phases.

The column extracts were isolated directly on 16.8-mL XAD-2 resin (see Fig. 3.3) that had previously been cleaned by successive Soxhlet extraction with water, methanol, acetone, and water. Each batch of resin was examined for nonpolar organic contaminants.

Organic compounds were eluted from the XAD-2 resin cartridge (used for batch extractions) with 15 mL of acetone and 5 mL of methylene chloride (60 mL acetone and 20 mL methylene chloride was used for the column cartridge). Solvent containing the eluted material was then concentrated to 1 mL using a Kuderna-Danish (K-D) evaporator. The extract containers were rinsed with the eluting solvent prior to desorption of the resin.

An exception to the above procedure was made in the filtration study (Section 3.2.3). In this case resin from each XAD-2 cartridge (through which a column extract had passed) was emptied into a 150-mL beaker. Fifty milliliters of acetone/methylene chloride (50/50 mixture) were added, and the mixture was placed in an ultrasonic bath for 15 min. A 1-mL aliquot was removed and spiked with azulene as an internal standard. This aliquot was analyzed by gas chromatography.

Aliquots (500 mL) of all other aqueous extracts were spiked with azulene, adjusted to pH 12 with NaOH, and extracted three times with 50 mL methylene chloride. The pH was then adjusted to pH 2 with HCl and extracted three times with 50 mL methylene chloride. The methylene chloride extracts were combined, dried over anhydrous sodium sulfate, and reduced in volume using a K-D evaporator. The standard solutions were reduced to 1 mL and the solid waste extracts to 10 mL, since higher levels of organic compounds were present in the solid waste extracts. In all cases, the final concentration of the internal standard was 10 ppm. The extracts were analyzed by gas chromatography. One solid waste extract was also analyzed by gas chromatography/mass spectrometry to confirm the presence of the identified compounds.

The organic concentrates were analyzed by gas chromatography using fused silica capillary columns (30-m-long x 0.25-mm-i.d. columns coated with SE-52 stationary phase from J&W Scientific). Gas chromatography was performed using a Hewlett-Packard Model 5736A gas chromatograph with a Model 18835B Grob-type split/splitless injection system. The splitless injection technique was used throughout this work.

Quantitation was obtained using a Hewlett-Packard Model 3390A recording integrator. Gas chromatography/mass spectrometry was performed using a Hewlett-Packard Model 5985 gas chromatograph/mass spectrometer/data system in the electron impact mode. Volatile organic compounds in selected extracts were isolated by purge and trap procedures (Zlatkis et al. 1981) and analyzed by gas chromatography, as above. The combustion-infrared method (EPA 1979b) was used to determine dissolved organic carbon (DOC) concentrations. The ORNL in-house quality assurance program, which was used throughout this study, indicates a coefficient of variation of less than 8% by this DOC method.

3.3.3 Mutagenicity testing

Mutagenicity testing was carried out under both Tasks 1 and 2. Under Task 1, the _Salmonella_/microsome mutagenicity assay was applied in an abbreviated screening mode to Soxhlet isolates, acid/base/neutral fractions obtained through sequential extraction, and the five aqueous extraction procedure extracts generated from Task 1. The general methodology for the _Salmonella_/microsome assay has been described elsewhere (Epler et al. 1980). In a screening mode, this assay is restricted to two _Salmonella typhimurium_ strains: TA100, with a _hisG_ base-pair substitution, _uvrB_ and _rfa_ factors, and the pKM101 plasmid; and TA98, the _hisD_ frameshift, also carrying the _uvrB_ and _rfa_ factors and the pKM101 plasmid. The tested strains were used without metabolic activation as well as with addition of microsomal preparations from both phenobarbital and Aroclor-1254-induced rats (henceforth referred to as phenobarbital activation and Aroclor activation).

Organic concentrates were prepared by methods identical to those used for chemical analysis (Section 3.3.2) except that the isolates were dried under a nitrogen stream. The residue was then dissolved in 2 mL of dimethylsulfoxide (DMSO).

Under Task 2, the two sample preparation protocols (Section 3.2.4, Section 4.2) were compared using the Ames test (the full five-strain Ames plate assay procedure, with and without metabolic activation) on solid waste leachates and wastewaters. The general methodology has been described elsewhere (Epler et al. 1980). This procedure was slightly modified to conform to the EPA/NEIC protocol (EPA 1980c) for conducting the *Salmonella*/microsome assay. The criterion used of "positive" test was the modified two-fold rule, i.e. a positive dose-response with a revertant value--for at least one of the test material doses--at least twice that of the spontaneous revertant value (solvent control).

3.3.4 Analysis of Bioaccumulative Materials in Wastes and Leachates

Soxhlet isolates, acid/base/neutral fractions obtained through sequential extractions of the wastes, as well as organic concentrates from the five aqueous extraction procedures were tested for bioaccumulation potential (EPA 1978) in Task 4.

Basically, the method involves chromatography of a series of compounds of known octanol/water partition coefficients on a reverse-phase HPLC system, using ultraviolet (UV) detection. When plotting the partition coefficient of known compounds against the log retention time, a straight line is obtained (as shown in Fig. 3.5) that can be used to extrapolate back to the partition coefficients of

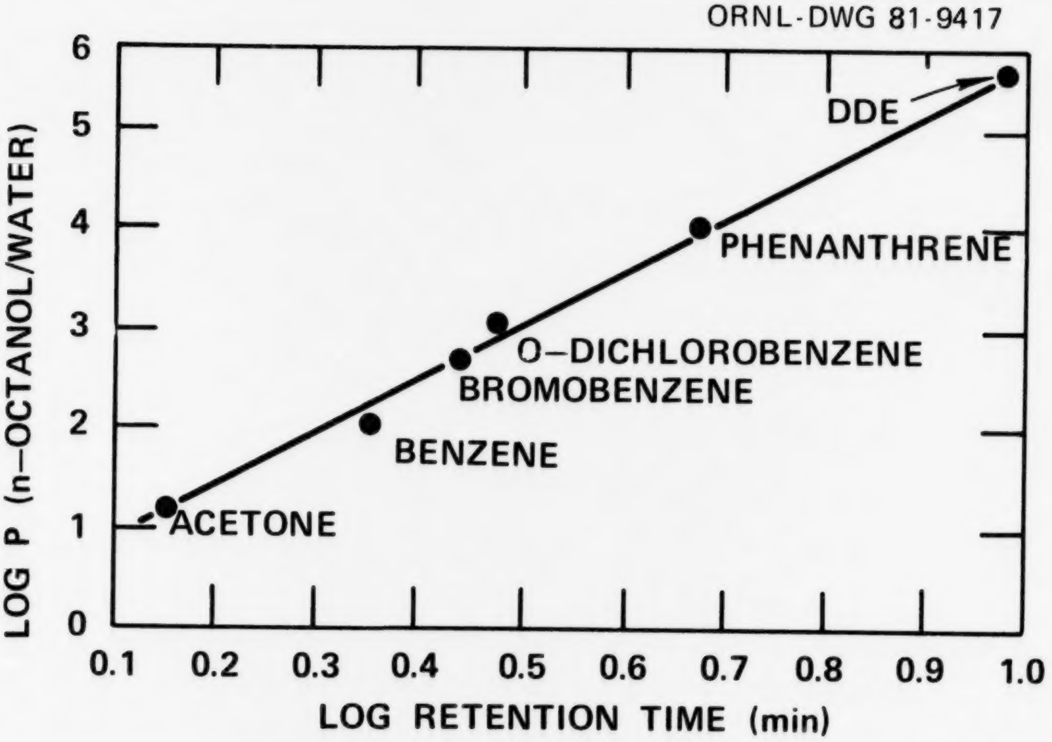

Fig. 3.5. Partition coefficients of known compounds plotted against log retention times.

unknown compounds. Constituents of an unknown mixture, having partition coefficients equal to or greater than log P = 3, are defined (EPA 1978a and 1978b) as being potentially bioaccumulative.

All samples were stored, refrigerated, at 4°C to avoid evaporation and decomposition. Each sample was injected onto a Zorbax® octadecylsilane column (4.6 mm x 25 cm) by use of a loop injector with a 20-μL sample loop. An 85:15 methanol-water mobile phase was degassed and pumped through the system using a Chromatix constant-flow pump at a rate of 1 mL/min. A Laboratory Data Control ultraviolet absorbance monitor at 254 nm was employed.

A standard solution was prepared using acetone, benzene, bromobenzene, orthodichlorobenzene, phenanthrene, and 2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene (DDE). The quantity of each compound was varied to produce peaks approximately 25% of the recorder scale (approximately 100 μg/mL). Preliminary standard runs were made with each compound in a 3:1 acetone-cyclohexane solution to determine optimum peak heights. The acetone-cyclohexane solution was diluted in the final standard with methanol to decrease the size of the acetone solvent peak while maintaining the solubility of the DDE.

Retention times of standard compounds were recorded each day. The bromobenzene peak was selected as an external standard for semi-quantitative comparison with sample peaks to account for day-to-day variation in instrumental response. Plots were made of log P (octanol/water partition coefficient) versus log retention time for extrapolation. The 500 to 1 concentration factor was used for aqueous extracts, with lower concentration factors applied to the waste isolates.

SECTION 4: RESULTS

4.1 Task 1: An Evaluation of Aqueous Extraction Procedures to Remove Nonpolar Organic Compounds from Solid Wastes

4.1.1 Inorganic Analyses of Extracts

The analytical results for selected inorganic components (NIPDWS metals) in the four batch extracts (EP, water, Na-resin, and citrate buffer) for wastes 1 through 6 are presented in Table 4.1. The citrate buffer extracts contained higher concentrations of all metals except for Ba in waste 1 and Cr in waste 4. In addition, Ba was present in the citrate buffer extracts in considerably higher concentrations than in the other batch extracts for wastes 2 through 6. The EP consistently produced extracts containing the second highest levels of metals (except Ba in waste 5). The water and Na-resin extractions yielded extracts containing comparable levels of metals.

All NIPDWS elements were analyzed in the water extracts of wastes 7 and 8 and the EP extract from waste 8 (Table 4.2). Neither of these wastes contained levels of metals that warranted further analyses of these wastes for inorganic constituents.

Inorganic analyses of the four batch extracts for wastes 9, 10, and 11 are presented in Tables 4.3, 4.4, and 4.5, respectively. Three EP extractions were performed on sample 10 for the organic isolation study (Task 2, see Section 3.2.4) to produce necessary quantities of extract. The three extracts were analyzed separately for inorganic elements.

Extracts from wastes 9, 10, and 11 were also examined for Fe, Ni, and Zn, because such coal-related wastes are expected to contain these

TABLE 4.1. SELECTED INORGANIC ANALYSES OF EXTRACTS PRODUCED USING FOUR EXTRACTION PROCEDURES FOR WASTE SAMPLES 1-6

		Extraction procedure[a]			
Waste	Element	EP	Water	Na-resin	Citrate buffer
		μg/L			
1	As	65,000	37,000[b]	84,000[b]	156,000[b]
	Ba	150	79	100	35
2	Ba	144 ± 51[c]	310	210	730
	Cr	3,940 ± 1,216[c]	131	180	17,400
3	As	3.0	0.54	0.8	21
	Ba	660	590	390	990
	Cr	18	8.9	1.3	510
4	Ba	400	460	190	1,100[a]
	Cr	180	163	160	34
5	Ba	1,500	470	190	1,430
6	Ba	650	460	430	3,000

[a] Single determination.

[b] Exceeds EP threshold concentrations as in 40 CFR 261.24.

[c] Mean and standard deviation of replicate extractions (n=2).

TABLE 4.2. INORGANIC ANALYSES OF WATER AND EP EXTRACTS FOR WASTES 7 AND 8

Element	Water extraction[a]		EP[a]
	Waste 7	Waste 8	Waste 8
	μg/L		
Ag	<0.01	<0.01	<0.01
As	4.7	0.4	2.9
Ba	210	520	370
Cd	0.13	0.63	0.91
Cr	2.6	2.2	13
Hg	0.008	0.004	0.02
Pb	4.1	2.1	11
Se	<0.5	<0.5	<1

[a] Single determination.

TABLE 4.3. INORGANIC ANALYSES OF EP, WATER, NA-RESIN, AND CITRATE BUFFER EXTRACTS FOR WASTE 9

Element	Extraction procedure[a]			
	EP	Water	Na-resin	Citrate buffer
	µg/L			
Ag	<0.1	<0.1	<0.1	nd[b]
As	1.7	0.65	3.0	13
Ba	160	120	130	600
Cd	0.73	<0.02	<0.02	nd
Cr	2.6	0.51	0.56	98
Hg	0.04	nd	nd	nd
Pb	2.6	0.99	2.0	nd
Se	1.8	<2	2.3	5.0
Fe	4.0	8.1	22	16,300
Ni	5.9	<1	<1	140
Zn	543	70	15	3383
$SO_4^=$	69,000	70,000	nd	nd

[a] Single determination.

[b] nd = not determined.

TABLE 4.4. INORGANIC ANALYSES OF EP, WATER, NA-RESIN, AND CITRATE BUFFER EXTRACTS FOR WASTE 10

	Extraction procedure			
Element	EP[a] ($\bar{x}$ ± S.D.)	Water[b]	Na-resin[b]	Citrate buffer[b]
	μg/L			
Ag	38[c]	<0.1	<0.1	0.28
As	8.3 ± 1.6	0.7	0.6	3.6
Ba	147. ± 5.8	160	130	170
Cd	<0.1	<0.1	0.67	1.8
Cr	5.4 ± 2.5	3.8	6.7	42
Hg	0.06[b]	nd[d]	nd	nd
Pb	16.5 ± 13.4	11	8.7	43
Se	4.6 ± 0.8	4.9	4.3	12
Fe	11 ± 7	8.8	4.4	16,500
Ni	25 ± 4	21	46	62
Zn	30 ± 27	19	7.5	63

[a] Three extractions were performed. Values (means and standard deviations) reported are based on single determinations on each of the the 3 extracts.

[b] Single determination.

[c] Highest value reported, all other values less than detection limit.

[d] nd = not determined.

TABLE 4.5. INORGANIC ANALYSES OF EP, WATER, NA-RESIN, AND CITRATE BUFFER EXTRACTS FOR WASTE 11

	Extraction procedure[a]			
Element	EP	Water	Na-resin	Citrate buffer
	µg/L			
Ag	0.03	0.05	0.16	0.42
As	0.3	0.5	1.2	225
Ba	335	306	222	777
Cd	0.97	0.38	0.24	5.2
Cr	<0.7	<0.7	<0.7	483
Hg	<0.01	nd[b]	nd	nd
Pb	1.4	1.3	<1	263
Se	<0.5	<0.5	<0.5	1.8
Fe	1,830	320	45	83,000
Ni	130	70	7	330
Zn	220	84	9.6	570

[a] Single determination.

[b] nd = not determined.

metals. Extract data for wastes 9, 10, and 11 showed consistently higher concentrations of metals in the citrate buffer extracts. In several cases (Cr in sample 9, Se in sample 10, and As, Cr, and Pb in sample 11), the citrate buffer extraction produced levels in excess of the NIPDWS concentrations. In general, higher concentrations of Ba, Cd, Cr, Pb, and Se were noted in the citrate buffer extracts.

The higher extraction efficiency for metals by the citrate buffer extraction may be explained in part by the large quantities of Fe released with this extractant (Table 4.6). The high complexing capacity of citrate for Fe tends to solubilize Fe from iron-solid phase matrices, thus releasing associated metals from the solid phase.

4.1.2 Isolation of Organic Compounds from Wastes

The isolates produced by the Soxhlet extraction and the three-step sequential extraction procedure were compared by gravimetry as well as by gas chromatography (see Section 3.2.1). The gravimetric data are shown in Table 4.7. The three-step sequential extraction scheme consistently extracted more organic material from the wastes than did the Soxhlet. The major organic components of the wastes were isolated by both techniques. Figures 4.1 and 4.2 indicate the complexity of the waste isolates. For identification of the major organic compounds in the wastes, it was sufficient to analyze only the Soxhlet extracts by gas chromatography/mass spectrometry. Table 4.8 lists the compounds which were identified confidently in each of the waste isolates. In most cases where identifications were made, appropriate standards were not available, and identification was made by comparison with reference spectra. The compounds are listed in order of decreasing concentration.

TABLE 4.6. COMPARISON OF FE CONCENTRATIONS USING FOUR EXTRACTION MEDIA[a]

	Fe			
Waste	EP	Water	Na-resin	Citrate buffer
	mg/L			
1	0.009	0.001	0.001	25
2	0.12	0.059	0.070	10.5
3	1.55	0.41	0.14	8.7
4	0.035	0.037	0.013	0.51
5	0.77	0.036	0.028	3.3
6	0.99	0.24	0.076	32
9	0.004	0.008	0.022	16.3
10	0.01	0.008	0.004	16.5
11	1.8	0.32	0.045	83

[a] Single determination.

TABLE 4.7. TOTAL ORGANICS RECOVERED: COMPARISON OF SOXHLET EXTRACTION WITH THE SEQUENTIAL EXTRACTION SCHEME - GRAVIMETRIC DATA ON SOLID WASTE ORGANIC ISOLATES

	Sequential extraction			
Waste	Acids	Bases	Neutrals	Soxhlet
	- - - - - - - - mg/g of solid waste - - - - - - -			
1	0.74	4.4	38.4	12.1
2	2.4	0.15	14.9	3.0
3	6.5	0.2	24.0	1.3
4	3.5	0.1	58.2	21.0
5	1.6	0.2	26.6	14.2
6	1.0	0.2	60.6	11.2
9	2.7	0.24	368	151
10	0.25	0.4	16	4.1
11	0.48	0.31	344	25.8

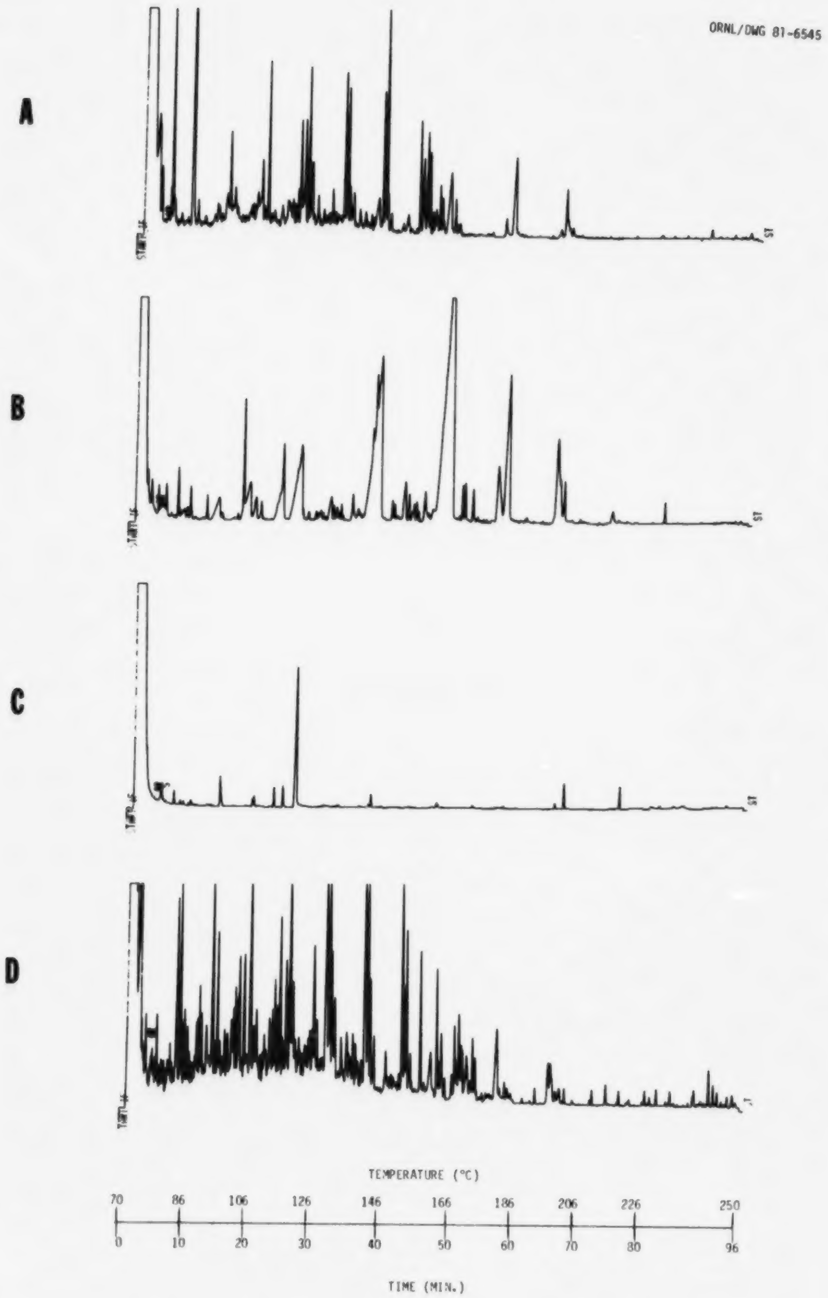

Fig. 4.1. Chromatograms for waste 2 - Soxhlet extract (A), and sequential extraction extracts: acids (B), bases (C), and neutrals (D). Injection temperature - 300°C, detector temperature - 300°C, carrier gas - H_2 at 1.2 mL/min.

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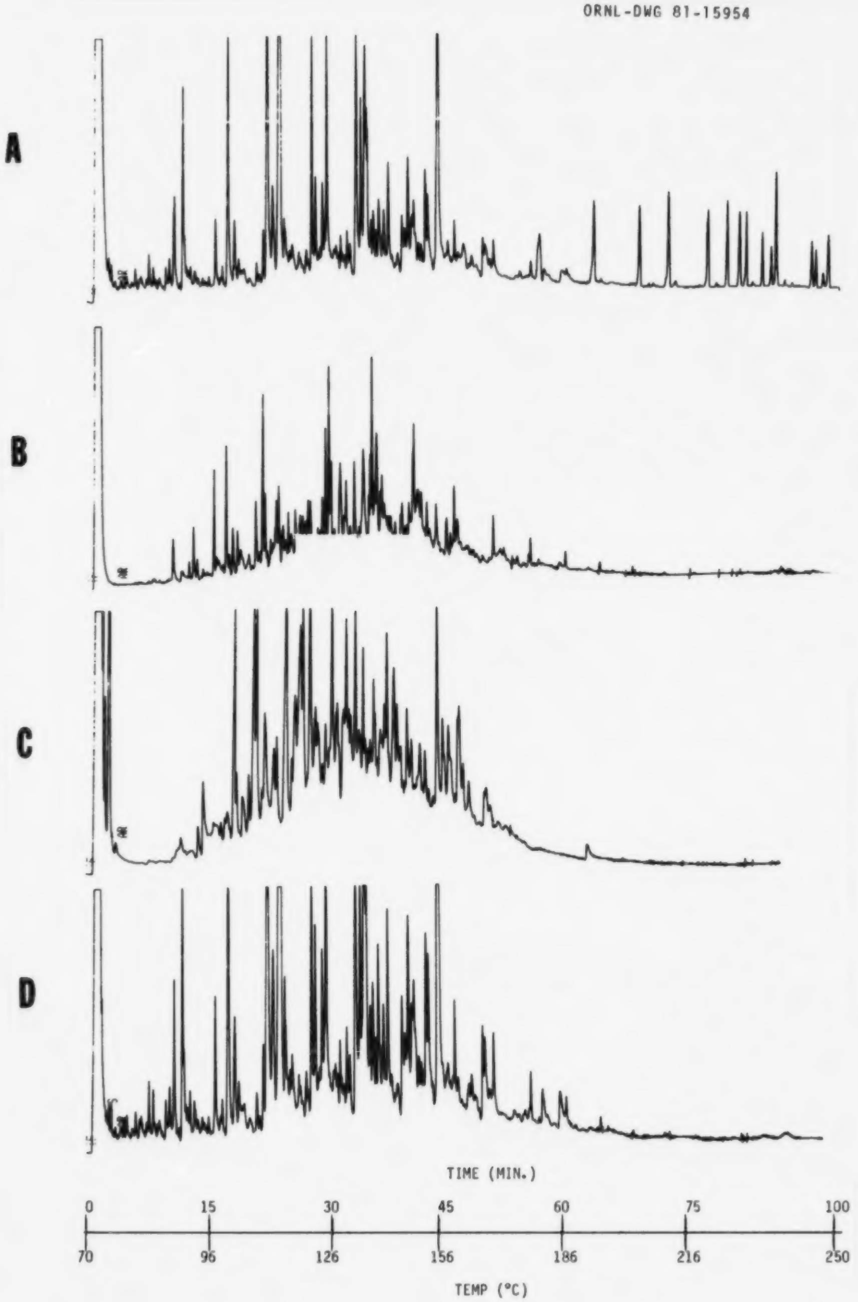

Fig. 4.2. Chromatograms for waste 11 - Soxhlet extract (A) and sequential extraction extracts: acids (B), bases (C), and neutrals (D). Conditions as in Fig. 4.1.

TABLE 4.8. ORGANIC COMPOUNDS IDENTIFIED IN SOLID WASTES[a]

Waste	Compounds
1	Nitroaniline[b]
2	Hydrocarbons (19)[c], cresol[b], indole[b], methyl indoles (2)[c], phthalates (3)[c], nonyl phenols (5)[c], decanoic acid, phenanthrene[b]
3	Aliphatic hydrocarbons, cresol[b], naphthalene[b], hydroxy indole
4	Tributyrin, *o*-hydroxy benzaldehyde (2)[c], methylene bisphenol (2)[c], hydroxy benzyl alcohol, phenol[c], hydroxy benzoic acid, biphenol (2)[c], fluoranthene[b], bicresol (Tentative), piperonal
5	Aliphatic hydrocarbons, cresol[b], methyl indole, hydroxy indole, methoxy indole
6	Aliphatic hydrocarbons, siloxanes, dioctylphthalate[b], cresol[b], indole[b], dibutylphthalate[b], methyl indole, butyric acid, phenyl acetic acid, octanoic acid, decanoic acid
9	Methyl fluoranthene[b], methyl biphenyl[b], trimethylnaphthalene,[b] biphenyl[b], various aliphatic hydrocarbons
10	Biphenyl[b], C_5 phenol, C_1 tetrahydronaphthalene, C_1 naphthalene (2)[b], tetrahydronaphthalene, minor components, C_3 hydroxy biphenyl C_2 biphenyl (2)[c], isopropyl cyclohexane, C_3 benzenes (3)[c], indane, naphthalene,[b] hydroxy anthracene, acenaphthene[b], C_{11} biphenyl, dibenzofuran, fluorene, phenanthrene[b], hydroxy fluorene, C_1 phenanthrene (2)[b,c], methoxyphenanthrene
11	Biphenyl ether, biphenyl[c], phenanthrene[b], tetrahydronaphthalene, cresol[b], C_3 phenol, xylenols (3)[c], phenyl phenol, tolyl phenol (5)[c], C_5 phenol, bipiyridyl, acridine + benzoquinolines, dibenzofuran, acenaphthene[b], fluorene[b], dibenzothiophene[b], phenanthrene[c], fluoranthene[b], pyrene[b]

[a] Compounds identified in Soxhlet isolates in order of decreasing concentration.

[b] Comparison with authentic standards.

[c] Number of isomers detected.

Comparison of the gravimetric data with the total area of the chromatogram indicated that 15 to 20% of the mass was eluted under these chromatographic conditions.

The organic content of the wastes varied considerably, as was expected, although wastes 2, 3, 5, and 6 contained similar compounds, predominantly hydrocarbons and carboxylic acids. The acids in these wastes probably resulted from decomposing municipal refuse (these wastes were obtained from landfills that also received municipal waste), while the hydrocarbons may have resulted from oil disposal. Waste 1 contained nitroaniline, which constituted about 99% of all organic material present. Waste 4 contained exclusively phenolic compounds plus tributyrin. These compounds resulted from a phenoxy resin plastic manufacturing process. Wastes 9, 10, and 11 contained similar compounds; each waste resulted from a coal conversion process. Thus, the major constituents of these wastes are phenols, aromatic heterocycles, and aromatic hydrocarbons.

Volatile organic compounds were determined (see Section 3.2.1) for wastes 2, 3, and 9 (Figs. 4.3 and 4.4). Volatile compounds included hydrocarbons, phenols, and sulfur compounds. Figure 4.3 shows that volatile compounds from waste 2 could be detected after aging 4 years in a carefully covered landfill.

4.1.3 Organic Analyses of Aqueous Extraction Procedure Extracts

4.1.3.1. Dissolved Organic Carbon Results

Earlier studies of solid waste extracts (from batch extraction procedures) indicated that a screening procedure for the presence of water-soluble organic compounds would be desirable (Epler et al. 1980).

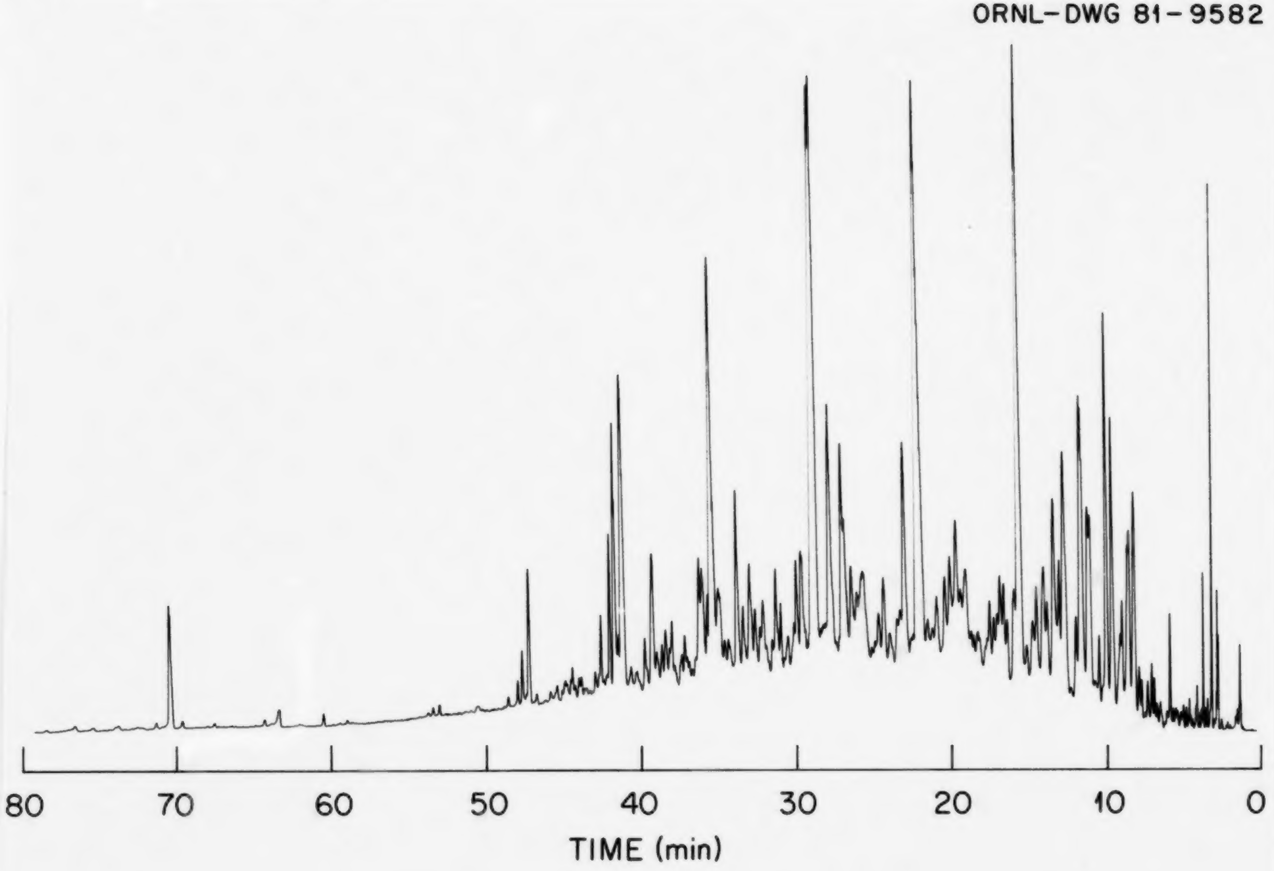

Fig. 4.3. Chromatogram of waste 2 (aged four years in a tightly covered landfill) - volatile organic compounds. Conditions as in Fig. 4.1.

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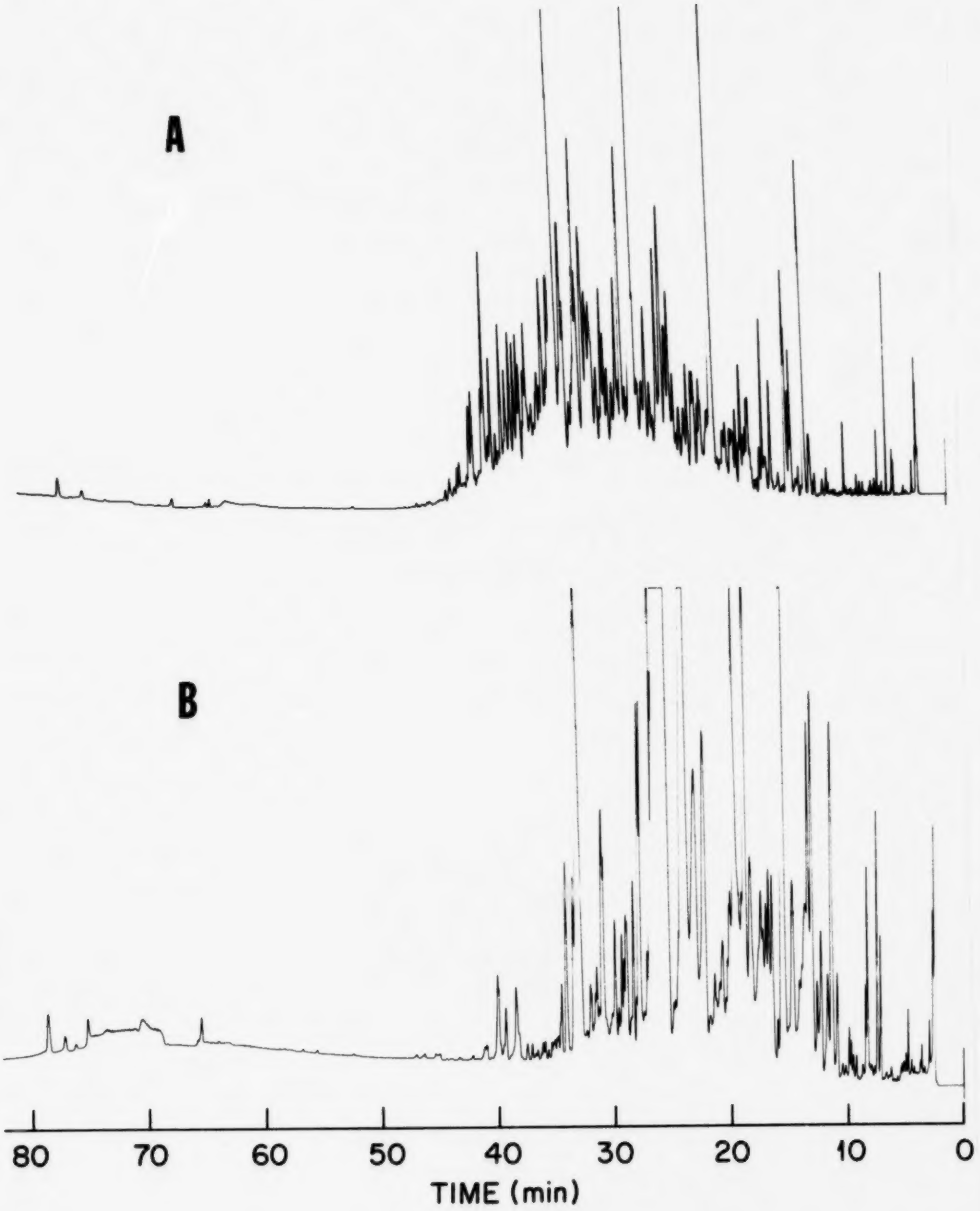

Fig. 4.4. Chromatograms of volatile organic compounds for waste 3 (A) and waste 9 (B).

Such a screening protocol would reduce the laboratory time for preparing and analyzing extracts for organic constituents. Dissolved organic carbon (DOC) analysis is an appropriate method for screening extracts for organic constituents. However, it cannot be used for extraction procedures that use organic acids (e.g., acetic acid used in the EP or citric acid) unless very high concentrations of other organic compounds are present above the acid background levels in the extract.

The water and Na-resin batch extracts were also examined for DOC concentrations. In addition to the batch procedure extracts, the column extracts, after passing through XAD-2 resin, were analyzed for DOC to screen for organic compounds not retained by the XAD-2 resin (e.g., very polar organic compounds).

The concentrations of DOC found in extracts of the water, Na-resin, and column (after passing the XAD-2 resin) procedures for the 11 wastes tested are shown in Table 4.9. All wastes contained detectable quantities of organic components. There was no significant statistical difference in quantities of DOC extracted between the water and Na-resin procedures (SAS Institute, Inc. 1979). Although the column extracts were not analyzed for the specific organic compound present, previous studies with XAD-2 resin indicate that polar compounds, e.g. dicarboxylic acids, nonextractable with organic solvent accounted for the levels of DOC observed (Epler et al. 1980). Column extracts from waste 14 did not contain extractable organic compounds above 10 μg/L (Section 4.1.3.2).

As DOC analysis requires filtration at the submicron level, it was necessary to evaluate the effect of filter type. Therefore, all water

TABLE 4.9. DISSOLVED ORGANIC CARBON (DOC) OBSERVED IN SELECTED AQUEOUS WASTE EXTRACTS[a]

	Extraction		
Waste	Water	Na-resin	Column - after passing through XAD-2
	mg/L		
1	198	155	80
2	457	494	206
3	207	178	246
4	254	353	319[b]
5	92	64	268
6	552	406	423
7	134	37	ne[c]
8	42	48	ne
9	13	13	10
10	54	39	50
11	46	28	nd[d]

[a] Filtered through glass fiber filters (Whatman GF/F, precombusted 0.7 μm).

[b] Average of two replicates.

[c] ne = not extracted.

[d] nd = not determined.

and Na-resin suspensions were filtered using two types of filters: a polycarbonate membrane filter (Nuclepore, 0.4 μm) and a precombusted glass-fiber filter (0.7 μm). The glass-fiber-filtered extracts were expected to be higher in DOC due to sorption of organics on polycarbonate filters as well as passage of submicron particles (0.4-0.7 μm) through the glass fiber filter. However, as Table 4.10 shows, this was generally not the case. In cases where large (order of magnitude) differences were found in DOC values (e.g., the Na-resin extracts from wastes 3 and 9), the polycarbonate-filtered extracts contained the higher level. Statistical analysis (SAS Institute, Inc., 1979) of data in Table 4.10 showed that there was no difference in DOC values between glass-fiber- and membrane-filtered extracts.

To determine whether changes in the DOC values during the 24-h extractions, warranted consideration of a shorter extraction time, 25-mL aliquots (one aliquot for each sampling time) were drawn from the extraction vessel immediately after the wastes were thoroughly mixed and at 1-, 2-, 4-, 8-, and 24-h intervals. Figures 4.5 and 4.6 graphically describe concentrations of DOC found in the water and Na-resin extracts, respectively. These plots show there was no consistent pattern of increase or decrease in DOC values with respect to time. In general, the wastes that contained appreciable levels of volatile organics (wastes 2 and 3) decreased in concentrations of DOC over the extraction time. This phenomenon might be expected because the extraction vessel was not sealed.

TABLE 4.10. COMPARISON OF DOC IN EXTRACTS FILTERED THROUGH GLASS FIBER AND POLYCARBONATE FILTERS

Waste	Water extracts		Na-resin Displacement extracts	
	GF[b]	NF[c]	GF[b]	NF[c]
	mg/L			
1	198	212	155	124
2	457	505	494	437
3	207	337	178	1740
4	254	243	353	280
5	92	72	64	44
6	552	544	406	480
7	134	29	37	30
8	42	45	48	42
9	13	10	13	110
10	54	56	39	40
11	46	49	28	46

[a] Single value determinations.

[b] Glass fiber filter (Whatman GF/F, precombusted, ≈0.7 μm).

[c] Polycarbonate filter (Nuclepore, 0.4 μm).

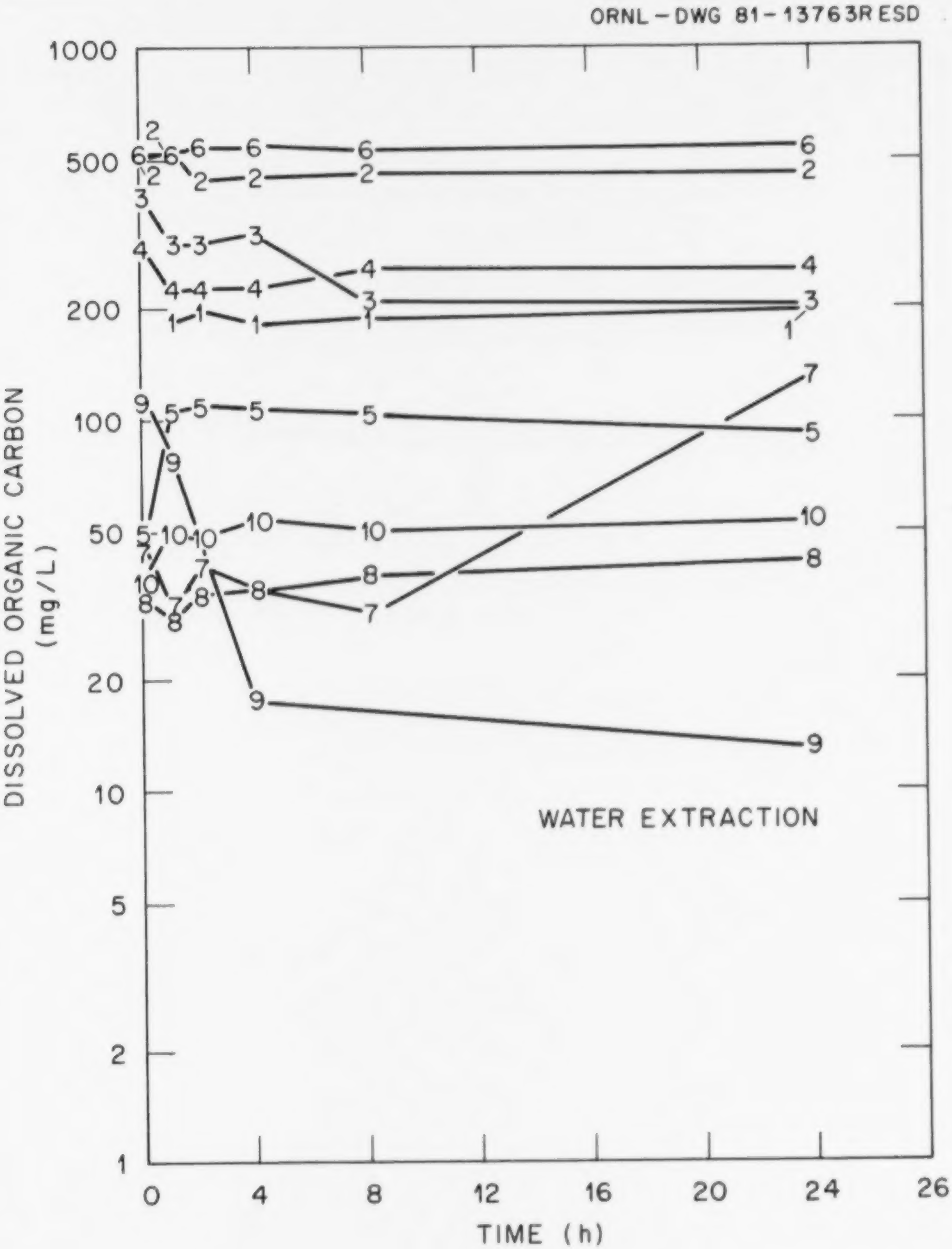

Fig. 4.5. DOC found in water extracts over the 24-h extraction time.

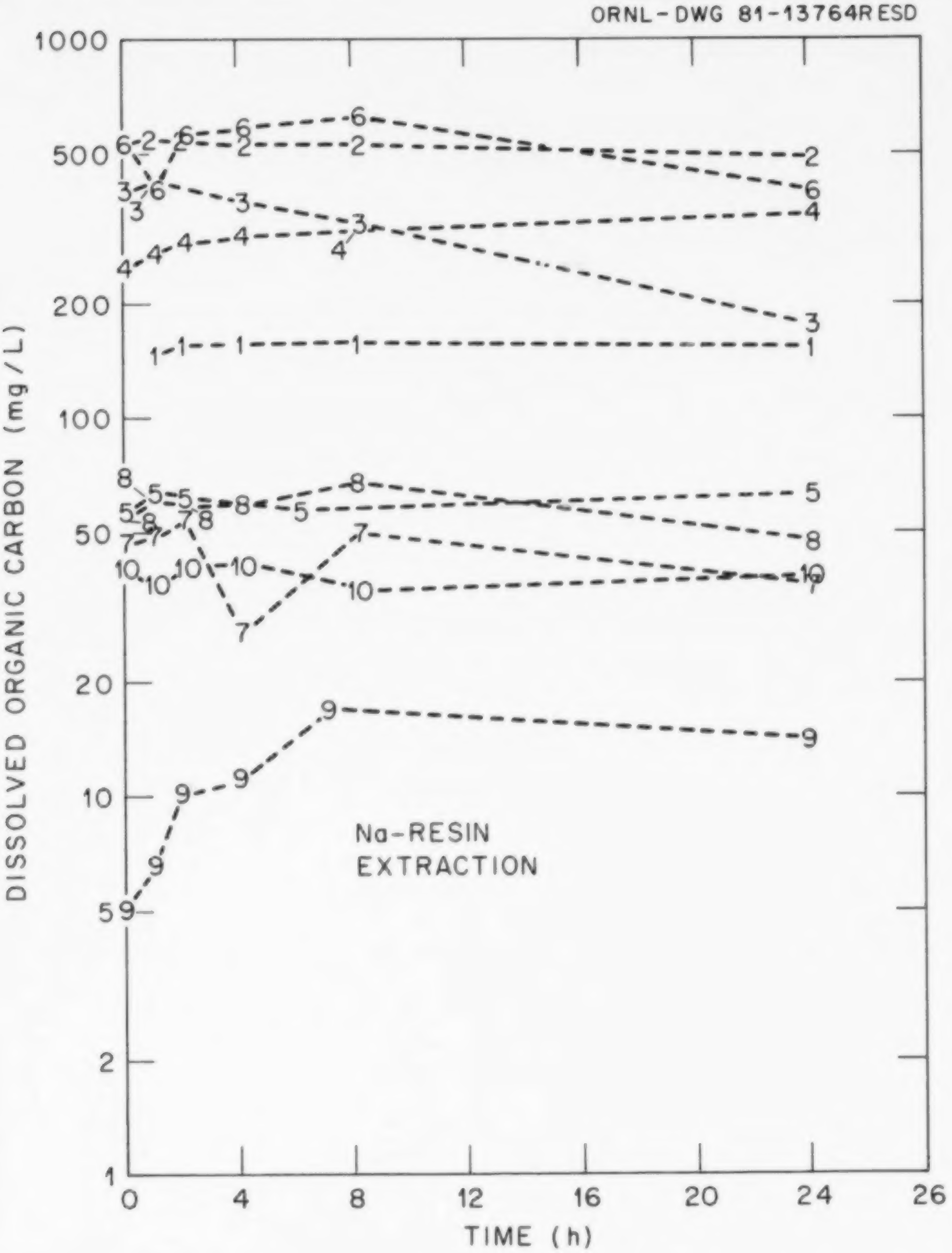

Fig. 4.6. DOC found in Na-resin extracts over the 24-h extraction time.

Because the DOC values changed over time for each sample, a linear regression analysis was performed to determine if these changes were significant over time (SAS Institute, Inc. 1979). The following waste extracts showed a statistically significant change ($P < 0.05$) in DOC (slope of linear regression different from zero) over the 24-h extraction time:

(1) the water extracts from wastes 7 and 8 increased in DOC over time,

(2) the Na-resin extract from waste 4 increased, and

(3) the Na-resin extracts from wastes 2 and 3 decreased in DOC over time.

Although waste 9 did not show a statistically significant change over 24 h in DOC concentration by water extraction, there was a large drop in DOC concentrations (from 120 to 20 μg/L) in the first 4 h.

During the first 8-h of extraction, only the Na-resin extract from waste 9 increased in DOC. Overall, the majority of wastes extracted did not significantly change in DOC content over the extraction period. With the exception of the water extraction of waste 7, there were no significant differences observed between 8- and 24-h extraction times, suggesting that 8-h extraction may be as effective as the 24-h extraction, at least for the analysis of DOC.

4.1.3.2 Gas Chromatography and Gas Chromatography/Mass Spectrometry

Using GC and GC/MS analysis, the extracts produced from the five extraction procedures were compared in two ways. First, the total area of each of the chromatograms (excluding the solvent peak) was compared, as a measure of the total mass extracted. Because of the low levels of organic compounds present in most of the extracts, gravimetry was not useful. Second, the quantities of individual compounds extracted by the various media were compared. While it was not possible to obtain absolute quantitative data on the individual compounds, the equivalent treatment of all extracts ensures a reliable relative comparison. Blanks were run by carrying the media through all extraction and analytical operations. Appendix A contains quality control procedures used at ORNL for organic analyses as well as inorganic analyses.

The data for total chromatographable organic content for each of the extraction procedure extracts are shown in Table 4.11. Additionally, an estimate of the total chromatographable organic concentration is given for each EP extract. This estimate is based on average integrator response for aliphatic hydrocarbons and should only be used to make relative comparisons between samples.

To evaluate the relative effectiveness of the extraction procedures to extract organic compounds, each extraction procedure was ranked from lowest to highest (1 to 5) for each waste (Table 4.11). This ranking scheme was used to statistically detect significant differences ($P < 0.05$) among extraction procedures across wastes using a completely randomized design (by extraction procedure). Applying this ranking scheme, the following conclusions can be made relative to the effectiveness of the five extraction procedures to remove chromatographable organic compounds:

(1) The up-flow column was more aggressive than any of the batch extraction procedures.

TABLE 4.11. THE RELATIVE EFFECTIVENESS OF FIVE AQUEOUS EXTRACTION PROCEDURES TO REMOVE ORGANIC COMPOUNDS FROM SOLID WASTES

	Extraction procedure					
Waste	EP	Water	Na-resin	Citrate buffer	Column	Estimated total in EP (µg/L)
	- - - - - - - - - TCO vs EP (rank[a]) - - - - - - - - -					
1	1.0 (1)	3.1 (3)	8.7 (4)	2.6 (2)	22 (5)	328
2	1.0 (3)	0.79 (2)	1.4 (4)	0.10 (1)	6.7 (5)	224
3	1.0 (2)	0.5 (3)	0.32 (1)	2.0 (4)	7.3 (5)	31
4	1.0 (3)	1.1 (4)	0.84 (2)	0.45 (1)	6.3 (5)	340
5	1.0 (3)	3.6 (4)	0.07 (1)	0.14 (2)	4.1 (5)	700
6	1.0 (1)	37 (4)	2.6 (2)	4.2 (3)	49 (5)	6
9	0[b] (1)	1.0 (4)	0.42 (2)	0.44 (3)	4.7 (5)	37[b]
10	1.0 (3)	1.5 (4)	0.67 (1)	0.90 (2)	2.3 (5)	754
11	1.0 (4)	0.49 (2)	0.40 (1)	0.69 (3)	8.9 (5)	2740
Mean rank score[c]	2.33	3.33$^+$	2.00	2.33	5.00*	

[a] Ranking of each extraction procedure from lowest to highest (1 to 5) for each waste sample.

[b] Total in distilled water, as no detectable peaks were observed in the EP extract.

[c] Mean rank scores without the same superscript are significantly different ($P < 0.05$) by Duncan's multiple range test.

(2) Among batch extraction procedures, deionized distilled water was the most aggressive extracting medium.

(3) No statistical differences were observed among the EP, citrate buffer, and Na-resin batch extraction procedures.

The column extraction procedure was replicated three times using waste 10. The total chromatographable organic compounds (total area of the chromatographs as measured in integrator counts, a dimensionaless unit) for the three replicate column extractions were: replicate 1: 2.5×10^7, replicate 2: 2.7×10^7, and replicate 3: 3.2×10^7. The coefficient of variation associated with these three replicates was 13%. These data suggest that the extractions were in reasonably close agreement in terms of organic matter extracted. Chromatograms of the first and third extractions were quite comparable relative to organic compounds present (Fig. 4.7). Furthermore, the extract after passing through the resin cartridge was analyzed by the method described in Section 3.3.2 (solvent partition at basic and acidic pH). No extractable organic compounds were detected above 10 μg/L.

For individual organic compounds, data are shown in Table 4.12. Conclusions 1 and 2 developed above for total chromatographable organic compounds apply to individual compounds as well. Interestingly, it seems that the sample matrix is a major factor in individual compound differences between the four batch extraction procedure extracts. Cresol, for example, was extracted more effectively by the water procedure on wastes 2, 3, and 6, but by the EP on wastes 4 and 11.

Volatile organic compounds were also determined on selected samples. Figure 4.8 shows the results of the analysis of volatiles

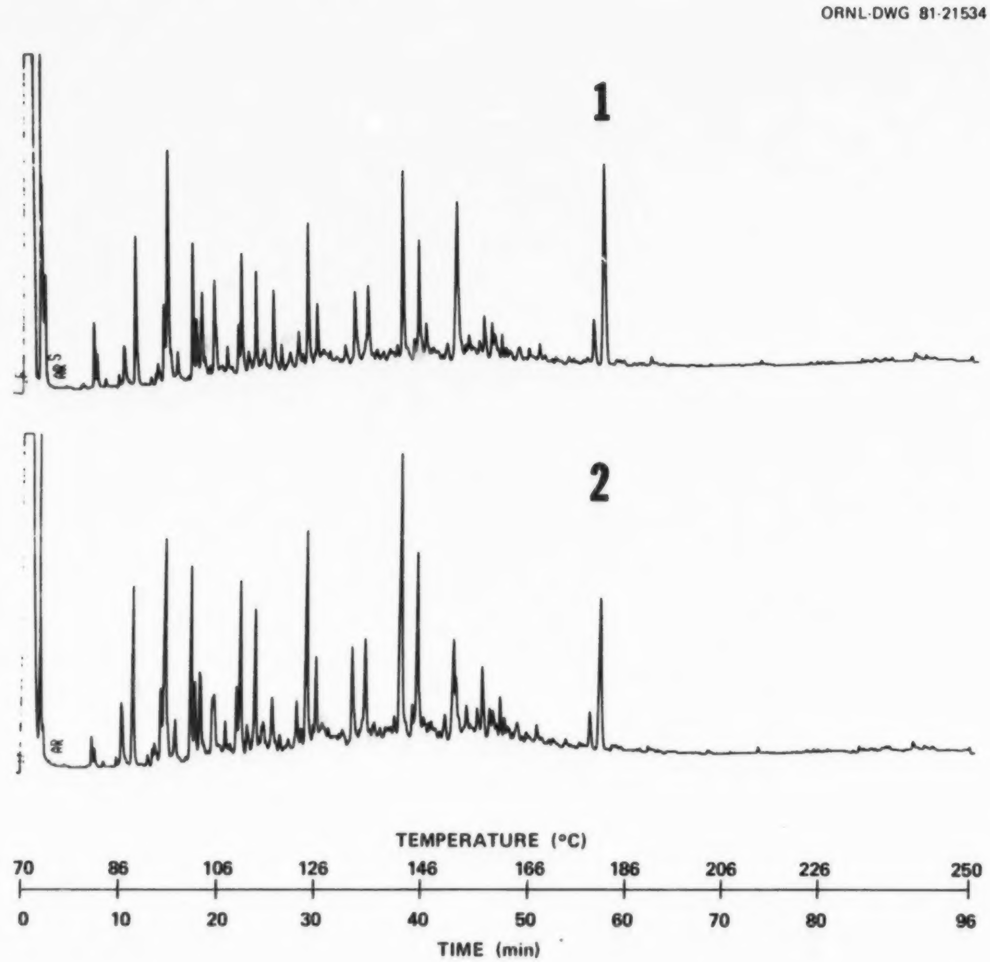

Fig. 4.7. Chromatograms of waste 10 column extracts - replicate 1 (1) and replicate 3 (2). Conditions as in Fig. 4.1.

TABLE 4.12. RELATIVE AMOUNTS OF INDIVIDUAL COMPOUNDS IN SOLID WASTE EXTRACTS AND RELATIVE RANKING OF THE EXTRACTION PROCEDURES

Waste	Compound	Extraction procedure[a]				
		EP	Water	Na-resin	Citrate buffer	Column
1	Nitroaniline	1.0	2.0	5.6	3.6	13
2	Cresol	1.0	1.6	1.0	0.02	36
	Indole	1.0	1.6	2.2	1.1	41
	Methylindole	1.0	0.76	1.1	0.98	14
	Decanoic acid	1.0	1.1	1.0	1.3	5.1
	Phenanthrene	1.0	2.0	1.8	0.58	21
3	Cresol	1.0	1.6	3.2	0.28	20
	Naphthalene	nd	1.0	nd	0.82	26
	Hydroxyindole	1.0	0.13	0.07	0.15	1.1
4	Phenol	1.0	2.2	0.88	1.6	21
	Cresol	1.0	0.72	0.91	0.55	12
	o-hydroxy benzaldehyde	1.0	1.0	0.20	0.96	2.3
	Tributyrin	1.0	1.6	1.8	1.6	3.6
	Methylene bisphenol	1.0	0.87	0.57	0.97	4.6
	Chrysene	1.0	15	16	7.4	16
5	Naphthalene	1.0	2.0	nd	nd	7.5
	Methylindole	1.0	2.0	nd	1.4	5.3
	Hydroxyindole	1.0	0.70	0.04	0.13	0.99
W						
	Methoxyindole	1.0	2.3	0.11	0.12	1.9
6	Phenol	nd	1	0.10	0.63	6.6
	Butyric acid	1.0	25	6.8	4.5	nd
	Cresol	1.0	12	1.3	6.3	1100
	Decanoic acid	1.0	16	8.5	9.7	22
	Phenyl acetic acid	1.0	49	1.6	1.8	51
	Indole	1.0	16	10	7.9	20
	Methyl indole	1.0	13	1.2	3.0	15
9	(No peaks identified)					
10	C_3 pyridine	1.0	4.7	3.1	3.9	13
	Naphthalene	1.0	3.2	1.4	1.6	15
	Quinoline	1.0	5.6	1.3	2.3	6.7
	1-methyl naphthalene	1.0	2.0	1.2	1.5	6.7
11	Cresol	1.0	0.33	0.68	1.3	15
	Xylenol	1.0	0.10	0.13	0.51	9.6
	Quinoline	1.0	0.52	1.1	0.74	4.3
	C_3 phenol	1.0	0.71	0.68	0.68	8.7
	Naphthol	1.0	0.70	0.51	0.58	8.8
	Biphenyl	1.0	3.5	2.8	0.85	17
Mean rank score[b]		2.08^{*}	$3.13^{\dagger}$	$2.44^{*\dagger}$	$2.49^{*\dagger}$	$4.87^{\ddagger}$

[a] nd = not detected.

[b] Mean rank scores without the same superscript are significantly different ($P < 0.05$) by Duncan's multiple range test.

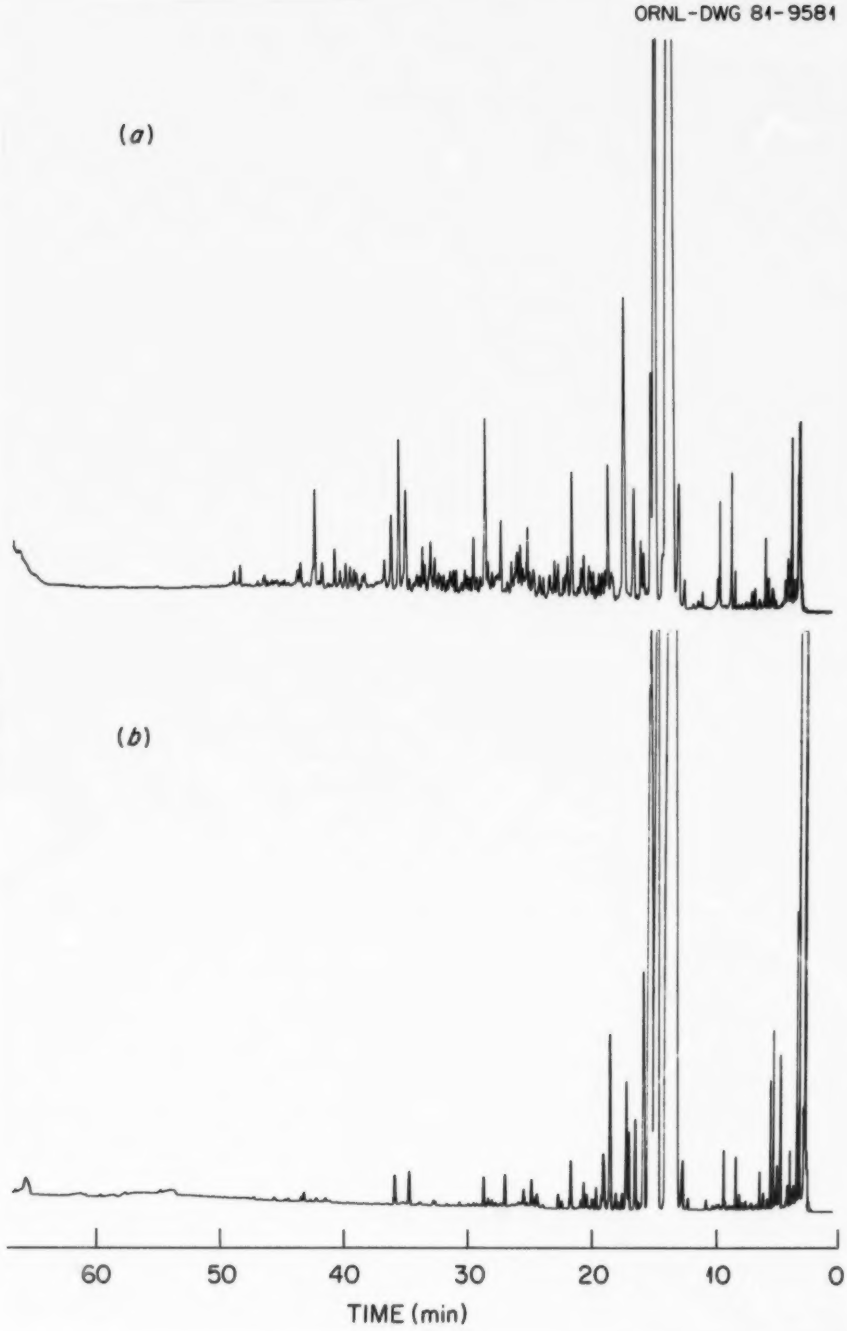

Fig. 4.8. Chromatograms of volatile organics from waste 2 extracts - citrate buffer extract (a) and Na-resin extract (b). Conditions as in Fig. 4.1.

from the citrate buffer extract and the Na-resin extract from waste 2. The citrate buffer extract clearly contained higher levels of volatile organic compounds. Similar results were obtained on wastes 3, 9, 10, and 11. While the mechanism of extraction of organic compounds using these two media was expected to be similar, there is a fundamental difference: the citrate buffer extraction is conducted in a sealed tumbler while the Na-resin extraction is conducted in a stirred vessel which is not airtight. To assess if the differences noted were actually due to the difference between the rotary extractor and the stirred vessels, or a result of the different extraction media, the distilled water extract of waste 2 was repeated in a sealed system. The results are shown in Fig. 4.9. The sealed vessel extract again contained much higher levels of organic volatiles, although not quite as high as in the citrate buffer extract, implying that both factors (vessel type and extracting media) are involved. Further examination of this phenomenon is recommended.

In summary, the column extraction procedure was found to be the most effective means of extracting nonpolar organic compounds. The most noticeable differences are in the levels of moderately volatile compounds (e.g., phenol and cresol) and in the levels of the nonpolar compounds (e.g., phenanthrene).

Factors contributing to the observed higher yields of organic compounds from the column procedure are:

(1) the column procedure is a closed system allowing for sorption of the moderately volatile compounds directly on the XAD-2 resin, and

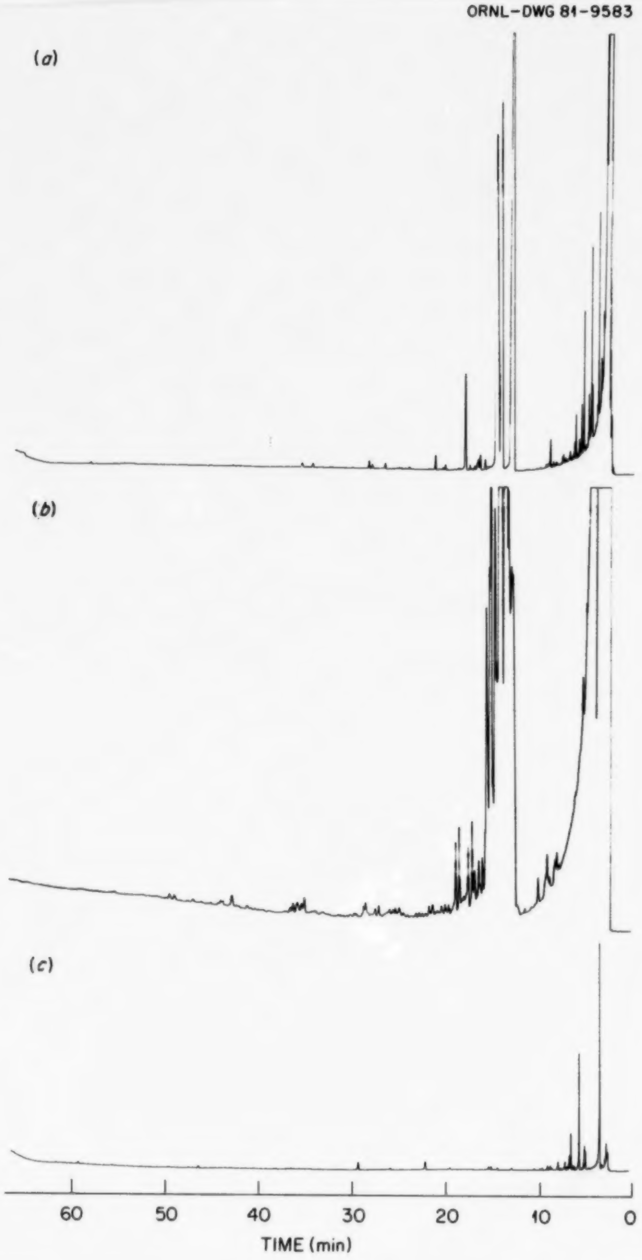

Fig. 4.9. Chromatograms of volatile organics in water extracts from waste 2 - open vessel (a) versus closed vessel (b), and distilled in glass water blank (c). Conditions as in Fig. 4.1.

(2) the column extracts were not filtered using membrane filters which are known to sorb appreciable quantities of nonpolar organic compounds (evidence relative to this effect is presented in Section 4.1.5).

It is important to point out that the major objective of this work was to develop an aqueous extraction procedure that simulated real-world conditions. The goal was to identify a procedure that was significantly better, in terms of removal of organic compounds, than the present EP, and one that could be used for a variety of wastes. The upflow column procedure appears to be such a procedure. However, the reasons for removal of greater quantities of organic compounds by this procedure are yet undetermined. Two of the contributing factors are suggested above. In a supplemental study, an experiment was conducted, using waste 14, to evaluate the influence of membrane filtering on column extracts.

The relative ranking of the extraction procedures to remove organic compounds from solid wastes (Tables 4.11 and 4.12) indicate that water is a significantly ($P < 0.05$) better extracting medium than the EP (acetic acid), Na-resin (sodium saturated system), or citrate buffer (0.5 M sodium citrate). It appears that a medium low in ionic strength, such as deionized distilled water, enhances solubilization and mobility of organic compounds from solid wastes. McKown et al. (1980) observed a similar solvent action with water. This solvent action in combination with the up-flow column procedure--which provides a continuous fresh supply of deionized distilled water--may be the primary mechanism responsible for the greater removal of organic compounds by the column procedure. Work in FY-1982 is intended to evaluate in greater detail the chemical mechanisms and/or operational processes that are responsible for the observed difference in quantities of organic compounds extracted by batch and column procedures.

The majority of the data presented here suggest that the physical apparatus, i.e. extraction vessel employed, has a greater effect on the organic content of the resulting extracts than the aqueous medium tested.

4.1.4 Mutagenicity Testing

For comparative purposes, the Salmonella/microsome assay results obtained with the various extracts from a given waste are reported together in Tables 4.13 - 4.21. The results of mutagenicity testing are summarized in Table 4.22. The modified two-fold increase rule was used as an indicator of positive mutagenic test response (EPA 1980c). A sample was considered toxic if in any test the background lawn was absent at two or more consecutive dose levels. As the presence of cytotoxicity can alter or mask the apparent mutagenic response, tests showing toxicity are noted.

Of the nine wastes examined (1-6, 9-11), seven were found to possess mutagenic activity in at least one extract or isolate. Only wastes 4 and 6 were without detectable genetic activity.

The results of mutagenic testing of waste 1 isolates and extracts are shown in Table 4.13. Among the aqueous extracts, a positive response was elicited, in the TA 98 strain of Salmonella typhimurium with the water, citrate buffer, and Na-resin extracts. The Soxhlet

TABLE 4.13. RESULTS OF MUTAGENICITY TESTING OF WASTE 1 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
Phenobarbital activation																		
75	T[e]	T	T	42	53	94	T	20	78	T	T	T	114	65	242	106	107	119
50	T	T	59	31	54	83	109	27	61	T	377	107	204	79	210	135	121	157
25	52	79	45	38	80	63	85	32	35	176	380	109	170	120	201	124	115	145
10	54	111	42	30	70	55	50	19	21	191	348	150	192	139	137	102	141	124
0	20	24	20	15	44	22	18	26	14	137	282	126	186	162	119	115	115	83
Aroclor activation																		
75	T	T	30	40	53	70	T	23	60	T	T	T	T	T	186	102	135	115
50	T	T	39	49	54	59	94	29	49	T	T	T	196	56	173	98	159	141
25	T	106	55	44	67	44	72	24	35	T	326	119	211	104	142	113	142	120
10	33	97	27	36	61	41	44	27	26	167	325	153	196	178	136	108	152	112
0	21	14	31	26	53	30	20	24	16	138	202	78	149	169	108	128	143	91
No activation																		
75						138									252			
50	T	T	T	28	17	62	150	22	32	T	T	T	148	T	199	119	106	99
25						60									167			
10						54									170			
0	14	21	20	19	45	20	19	31	29	163	166	142	177	167	144	107	137	91

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.14. RESULTS OF MUTAGENICITY TESTING OF WASTE 2 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
									Phenobarbital activation									
75	21	168	71	72	15	19	T[e]	15	32	74	153	107	149	T	59	T	120	113
50	18	154	71	44	16	10	16	17	36	81	290	120	169	T	69	T	106	121
25	15	165	29	42	27	20	12	17	18	73	308	94	169	148	93	T	94	82
10	20	137	19	28	26	29	10	16	18	80	220	83	83	142	103	117	107	106
0	17	151	21	16	16	16	22	20	26	94	226	86	112	141	93	150	99	119
									Aroclor activation									
75	27	71	52	34	29	20	T	26	32	85	227	T	T	T	T	T	98	120
50	29	99	40	39	27	24	T	15	32	82	193	156	142	T	T	T	107	128
25	23	82	29	32	30	21	13	14	26	94	188	194	92	T	T	T	86	113
10	23	67	32	30	32	18	19	18	24	86	215	125	78	149	T	T	113	124
0	19	74	30	17	18	18	32	15	23	133	178	119	200	125	114	153	122	115
									No activation									
50	19	20	15	18	19	6	T	20	33	93	141	117	94	T	T	T	121	114
0	22	28	8	16	42	14	15	16	14	99	194	104	200	120	119	179	106	141

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.15. RESULTS OF MUTAGENICITY TESTING OF WASTE 3 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
Phenobarbital activation																		
75	T	284	29	32	29	22	18	11	14	T	488	136	161	106	97	107	85	83
50	19	284	27	30	39	23	17	7	21	T	420	142	141	121	98	136	108	133
25	22	243	22	31	31	23	24	14	13	130	365	94	180	137	96	109	84	107
10	31	180	18	18	33	17	17	18	20	138	350	154	137	120	103	104	98	105
0	19	44	20	22	43	24	14	12	16	197	247	137	167	126	83	83	89	112
Aroclor activation																		
75	T	154	21	52	40	21	10	11	26	T	346	138	174	139	85	nd[f]	94	102
50	21	104	26	34	35	18	17	14	20	42	277	161	180	121	93	113	77	110
25	25	89	29	32	29	27	19	16	20	73	221	143	134	119	102	113	78	85
10	20	61	29	29	40	16	15	14	15	105	152	106	91	123	112	99	107	106
0	40	65	21	28	42	22	26	11	23	142	188	138	154	149	89	91	81	91
No activation																		
50	23	122	16	18	14	7	5	13	16	82	247	169	149	108	104	91	107	114
0	32	37	14	58	30	8	12	10	18	171	179	163	110	121	95	114	110	134

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

[f] nd = not determined.

TABLE 4.16. RESULTS OF MUTAGENICITY TESTING OF WASTE 4 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
Phenobarbital activation																		
75	14	163	38	18	16	T[e]	T	12	12	105	T	T	T	T	T	T	111	86
50	19	175	33	17	16	9	17	9	10	91	355	113	162	T	T	T	75	92
25	14	155	35	20	17	25	17	18	14	85	341	160	120	T	85	T	106	97
10	19	167	57	21	30	17	23	12	12	107	363	106	125	165	64	133	112	76
0	18	112	58	16	22	13	26	15	9	85	363	89	82	151	90	119	116	70
Aroclor activation																		
75	20	T	41	19	19	T	22	15	17	85	T	T	T	T	T	T	110	109
50	21	55	36	19	27	T	11	20	17	92	260	162	T	T	T	T	116	88
25	26	57	34	22	28	15	31	16	14	113	201	203	135	T	92	111	95	83
10	31	67	59	17	16	8	15	22	20	92	310	179	138	171	72	176	108	89
0	26	57	43	21	28	26	23	12	14	97	204	146	99	149	59	115	108	103
No activation																		
50	13	T	T	15	T	3	11	10	15	93	T	T	T	T	53	T	95	68
0	20	24	28	20	29	8	14	13	18	90	106	124	108	122	93	141	105	67

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.17. RESULTS OF MUTAGENICITY TESTING OF WASTE 5 EXTRACTS

Volume of DMSO test solution (μL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP^a	Water^a	Citrate buffer^a	Na-resin^a	Column^a	Soxhlet^a	Acid^a	Base^a	Neutral^a	EP^a	Water^a	Citrate buffer^a	Na-resin^a	Column^a	Soxhlet^b	Acid^c	Base^c	Neutral^d
Phenobarbital activation																		
75	15	154	74	50	18	34	22	110	15	75	362	129	185	122	111	94	166	61
50	13	165	58	47	22	35	20	63	13	83	335	158	178	160	135	114	178	56
25	21	180	42	13	18	35	18	46	11	98	404	188	146	153	113	83	182	68
10	12	164	67	30	18	25	16	33	12	74	249	133	163	136	159	115	172	66
0	18	85	51	30	32	15	14	22	9	85	322	123	148	141	109	83	150	70
Aroclor activation																		
75	18	85	76	43	34	22	24	24	15	99	229	T^e	154	162	109	104	150	55
50	22	82	53	21	29	32	24	25	16	105	253	94	135	154	150	99	151	54
25	18	87	44	34	28	22	15	37	11	94	215	71	146	160	95	107	190	72
10	21	91	42	29	30	25	20	32	10	107	216	99	127	148	117	115	137	75
0	26	83	25	37	29	21	26	32	14	97	268	79	113	180	97	91	153	103
No activation																		
50	20	30	24	46	19	17	10	24	6	96	180	119	T	117	110	110	121	62
0	12	29	22	37	29	18	18	15	18	90	238	121	186	165	121	134	179	67

[a] 250 μL of aqueous extract/μL of DMSO test solution.

[b] 1 mg solid waste/μL of DMSO test solution.

[c] 3 mg solid waste/μL of DMSO test solution.

[d] 300 μg solid waste/μL of DMSO test solution.

[e] T = toxic.

TABLE 4.18. RESULTS OF MUTAGENICITY TESTING OF WASTE 6 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP^a	Water^a	Citrate buffer^a	Na-resin^a	Column^a	Soxhlet^b	Acid^c	Base^c	Neutral^d	EP^a	Water^a	Citrate buffer^a	Na-resin^a	Column^a	Soxhlet^b	Acid^c	Base^c	Neutral^d
Phenobarbital activation																		
75	T	97	T	35	28	18	12	42	nd^f	T	T	T	169	138	57	63	106	nd
50	T	167	59	33	29	20	16	17	nd	T	T	T	160	137	89	136	126	nd
25	T	151	33	30	31	14	10	22	nd	T	334	T	119	169	86	130	90	nd
10	33	161	41	20	44	20	20	19	nd	138	328	T	191	168	82	86	108	nd
0	19	155	37	22	44	17	18	20	nd	128	352	116	167	220	60	115	118	nd
Aroclor activation																		
75	T	91	T	T	35	T	22	10	nd	T	T	T	T	163	99	T	88	nd
50	T	94	40	39	33	35	18	16	nd	T	T	T	T	192	82	T	102	nd
25	23	106	37	26	35	15	21	12	nd	T	219	T	160	240	60	80	103	nd
10	22	96	28	14	45	23	24	12	nd	135	239	136	180	243	88	103	75	nd
0	20	68	37	28	44	9	23	20	nd	138	233	113	154	227	61	119	75	nd
No activation																		
50	T	T	T	16	30	18	16	11	nd	T	T	T	70	118	43	81	81	nd
0	28	22	37	58	47	14	15	14	nd	116	169	186	110	136	109	123	96	nd

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

[f] nd = not determined.

TABLE 4.19. RESULTS OF MUTAGENIC TESTING OF WASTE 9 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
Phenobarbital activation																		
75	57	T[e]	43	45	7	41	65	T	57	206	160	174	161	86	T	T	187	162
50	40	41	38	48	13	33	58	53	43	187	162	215	167	61	T	T	187	165
25	64	33	55	39	8	41	60	41	35	202	181	226	165	70	117	227	150	163
10	61	46	44	53	16	47	52	71	32	191	165	217	175	74	112	220	216	135
0	48	40	48	40	17	17	47	47	19	168	216	201	216	117	104	173	173	174
Aroclor activation																		
75	37	T	48	45	T	T	T	46	54	193	187	234	T	T	T	T	207	173
50	42	39	39	32	18	T	T	52	40	177	206	199	167	99	T	T	160	160
25	39	44	49	39	15	T	T	46	30	199	160	174	182	78	T	T	188	151
10	55	46	47	42	14	47	39	59	32	162	165	173	205	91	107	231	205	163
0	69	41	42	41	18	27	28	28	20	188	152	175	152	118	98	182	182	98
No activation																		
50	35	20	51	30	T	T	T	26	33	220	121	207	163	T	T		204	92
0	54	34	43	34	6	29	35	35	28	233	191	229	191	82	192		192	103

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.20. RESULTS OF MUTAGENICITY TESTING OF WASTE 10 EXTRACTS

Volume of DMSO test solution (µL/plate)	Revertants/plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
									Phenobarbital activation									
75	T[e]	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	93	609	T	60	T	T	T	T	T	T	670	T	T
25	T	58	T	35	94	94	556	T	61	T	T	T	T	T	T	645	T	T
10	44	41	45	33	78	78	97	T	52	156	T	T	117	149	T	536	T	T
0	17	52	22	16	42	22	39	22	42	109	110	154	111	112	199	167	91	106
									Aroclor activation									
75	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
25	T	T	T	119	70	156	T	T	T	T	T	T	T	T	T	T	T	T
10	31	42	T	48	70	202	T	54	T	T	T	T	108	117	T	229	T	T
0	13	43	28	8	31	22	48	42	35	96	91	167	94	108	192	126	153	123
									No activation									
50	T	T	T	T	T	T	T	T	T	T	109	T	T	T	150	T	T	T
0	7	42	58	17	42	21	40	27	44	94	76	110	71	111	105	159	153	99

[a] 250 µL of aqueous extract/µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.21. RESULTS OF MUTAGENICITY TESTING OF WASTE 11 EXTRACTS

	Revertants/Plate																	
	TA 98									TA 100								
							Sequential extraction									Sequential extraction		
Conc. (µL/plate)	EP[a]	Water[a]	Citrate buffer	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]	EP[a]	Water[a]	Citrate buffer[a]	Na-resin[a]	Column[a]	Soxhlet[b]	Acid[c]	Base[c]	Neutral[d]
									Phenobarbital activation									
7.5	110	39	71	T[e]	T	T	17	232	T	T	T	163	119	T	T	T	205	T
5.0	92	52	57	45	T	T	17	161	T	T	71	213	109	T	T	120	160	T
2.5	46	45	54	46	17	T	17	57	T	117	136	169	125	T	T	109	176	
1.0	30	27	49	70	21	13	33	18	28	93	119	152	123	54	T	138	105	
0	19	16	42	22	20	27	26	21	21	85	80	150	106	62	113	107	104	71
									Aroclor activation									
7.5	98	74	80	T	T	T	26	125	T	T	T	156	151	T	T	T	T	T
5.0	59	52	86	T	T	T	46	68	T	T	T	165	109	T	T	T	T	T
2.5	53	27	48	110	14	T	20	35	T	T	78	214	182	58	T	119	T	T
1.0	29	29	39	97	29	14	34	19	T	78	79	176	143	48	T	140	T	T
0	20	18	40	29	26	22	20	41	15	65	74	135	110	73	45	94	202	47
									No activation									
5.0	7	9	42	27	T	T	T	21	T	T	95	120	T	T	T	T	T	T
0	4	7	30	22	18	3	15	15	8	40	30	95	85	46	122	65	90	116

[a] 250 µL of aqueous extract/1µL of DMSO test solution.

[b] 1 mg solid waste/µL of DMSO test solution.

[c] 3 mg solid waste/µL of DMSO test solution.

[d] 300 µg solid waste/µL of DMSO test solution.

[e] T = toxic.

TABLE 4.22. SUMMARY OF MUTAGENIC ACTIVITY OF SOLID WASTE ISOLATES: AQUEOUS EXTRACTS AND ORGANIC ISOLATES[a]

	Aqueous extracts					Organic isolates			
							Sequential extraction		
Waste	EP	Water	Citrate buffer	Na-resin	Column	Soxhlet	Acid	Base	Neutral
1	T	M	M	M	NE	M	M	NE	M
2	NE	NE	M	M	T	T	T	NE	NE
3	T	M	NE	NE	NE	NE	NE	NE	NE
4	NE	NE	NE	T	T	T	T	NE	NE
5	NE	NE	M	NE	NE	NE	NE	M	NE
6	T	T	T	T	NE	NE	T	NE	nt
9	NE	NE	NE	NE	NE	T	T	NE	M
10	T	T	T	M	M	M	M	T	T
11	M	M	NE	M	T	T	T	M	T

[a] NE = no effect, T = toxic, M = mutagenic, nt = not tested.

isolate, as well as the acid and neutral fractions from the sequential extraction, also gave a mutagenic response in TA 98. The Soxhlet isolate and the acid fraction were direct mutagens, whereas the remainder of the mutagenic extracts of this waste required metabolic activation.

Waste 2 displayed mutagenic activity in the citrate buffer and Na-resin extracts (Table 4.14). The positive response was confined to TA 98 and required metabolic activation. The column extract and Soxhlet isolate and the acid fraction from sequential extraction were toxic, particularly toward TA 100.

Mutagenic activity detected in waste 3 was restricted to the water extract (Table 4.15). Significant activity in TA 98 was noted with the phenobarbital-induced activation system, as well as in the absence of metabolic activation. Results obtained with TA 98 (Aroclor activation) and with TA 100 (with and without activation) treated with water extract support the positive observation noted with TA98/phenobarbital activated. No other extract or isolate elicited a mutagenic response.

As noted above, no mutagenic activity was observed with any of the isolate or extracts from waste 4 (Table 4.16). Toxicity was seen, however, with the Na-resin and column extracts, Soxhlet isolate, and the acid fraction from sequential extraction, which made mutagenicity impossible to detect.

Two samples from waste 5 gave a positive response with TA 98: the citrate buffer extract (with Aroclor activation) and the base fraction from sequential extraction (with phenobarbital activation) (Table 4.17). No other activities were noted; waste 5 extracts and isolates were essentially nontoxic in these assays.

No mutagenic response was observed with extracts and isolates of waste 6 (Table 4.18). Significant cytotoxicity was noted with the EP, water, citrate buffer extracts, and the acid fraction. The neutral fraction from sequential extraction was not available for testing.

Only one extract or isolate of waste 9 (the neutral fraction from sequential extraction) gave a positive mutagenic response (Table 4.19). This isolate was mutagenic in the presence of metabolic activation (either microsome preparation) in strain TA 98. The Soxhlet isolate and acid fraction were toxic.

Several samples from waste 10 were genetically active (Table 4.20). The Na-resin extract was mutagenic in TA 98 with Aroclor activation, while the Soxhlet isolate and column extract were active in TA 98 with phenobarbital activation. The data suggest that either activation system will accommodate the mutagenic agent(s) in these samples. A striking response was obtained with the acid fraction from sequential extraction. This fraction was mutagenic (with phenobarbital activation) in TA 98 and TA 100. All of the extracts and isolates from this waste were toxic at high dose levels.

The samples of the final waste assayed, waste 11, were sufficiently toxic that the dose range was lowered tenfold to bring survival up to a reasonable level for a meaningful assay (Table 4.21). The EP, water, Na-resin extracts, and the base fraction gave positive mutagenic responses in TA 98 with metabolic activation. The column extract, Soxhlet isolate, acid fraction, and neutral fraction were toxic. Even at an additional 10-fold reductions, the column extract was still toxic at the higher dose levels.

In summary, seven of the nine wastes possessed detectable mutagenic activity in one or more extracts or isolates (Table 4.22). It is interesting to note that the organic isolates produced by methylene chloride Soxhlet extraction and the three-step sequential extraction procedure showed mutagenic activity in two and five of the wastes tested, respectively. On the other hand, six of the nine wastes were found to possess mutagenic activity by using the less aggressive aqueous extracting procedures. The Na-resin extracts accounted for four of the seven positives. Water and citrate buffer revealed three of the wastes (but not the same three) to contain mutagenic activity while the EP and the column (which extracted the greatest quantities of chromatographable organic compounds) procedures revealed only one of the eleven wastes to contain mutagenic activity (again not the same waste). These data demonstrate the difficulties in establishing a single procedure or media that will be universally successful (with a broad variety of wastes) in providing an extract that allows unambiguous testing of mutagenicity. The sequential extraction procedures has the advantage of separating active components into separate fractions. In this way the confounding effects of cytotoxicity and mutagenicity are frequently resolved and information about the nature of the mutagen is obtained.

4.1.5 Filtration Study

One of the major objectives of the filtration study was to determine if the filtration of batch extracts (through 0.4-μm pore size membrane filters) was responsible for the large differences in concentration of organic compounds noted between the batch and column extraction procedures (the column extracts were not filtered using the 0.4-μm pore size membrane filters). To do this, a series of experiments were conducted as outlined in Section 3.2.3.

Small differences in amounts of organic compounds were found in the column extracts produced from experiments 1 and 2 (Table 4.23). In this experiment, the extracts were passed directly through XAD-2 resin, with and without an in-line glass fiber filter. These data suggest that entrained organic particles that can pass through the PTFE cloth i.e., < 10 μm, but would be retained by a glass-fiber filter i.e., > 0.7 μm, either do not represent a significant input to the XAD-2 resin or pass through it without being adsorbed with the waste tested (waste 14).

A column extract was also subjected to four separation treatments (Table 4.24). In this case, the glass fiber filter retained less organic material, judged by analyzing GC-elutable compounds in the filtrate, than did any of the other treatments. Compounds such as naphthol, phenanthrene, and benzo(a)anthracene were not detected in the extract filtered through the Millipore filter, nor was benzo(a)anthracene detected in the extract filtered through the Nuclepore filter. Thus, Millipore filters appear to be more sorptive for some classes of nonpolar organic compounds than do the Nuclepore filters. Sorption in this case appears to be related to filter type (material) rather than nominal pore size.

A comparison of the quantities of organic compounds found in the glass-fiber-filtered extracts collected directly from the column on XAD-2 resin (Table 4.23, approximately 25,500 μg/100 g) versus those

TABLE 4.23. ORGANIC COMPOUNDS FOUND IN COLUMN EXTRACTS, WITH AND WITHOUT AN IN-LINE FILTER[a]

Compound	Without filter	With filter[b]
	- - - - μg/100 g waste - - - -	
Naphthalene	945	1275
Quinoline	50	305
Naphthol	70	80
Dibenzothiophene	30	50
Phenanthrene	40	65
Benzo(a)anthracene	300	155
Total[c]	21,900	25,500

[a] Using waste sample 14, extracts collected directly from column on XAD-2 resin.

[b] Glass fiber filter (precombusted, Whatman GF/F, 0.7 μm) placed on top of column.

[c] Total = all elutable compounds using GC.

TABLE 4.24. ORGANIC COMPOUNDS REMAINING IN A COLUMN EXTRACT AFTER USING FOUR SOLID/LIQUID SEPARATION TREATMENTS[a]

	Filtered			
Compound	Glass fiber (0.7-μm)	Nuclepore (0.4-μm)	Millipore (0.45-μm)	Centrifuged[b]
	- - - - - - - - - μg/100 g waste - - - - - - - - -			
o-cresol	9648	1948	1632	1496
Naphthalene	5052	2756	2228	2108
Quinoline	1376	412	428	400
Naphthol	392	80	nd[c]	72
Dibenzothiophene	336	64	68	28
Phenanthrene	400	76	nd	44
Carbazole	104	76	168	40
Benzo(a)anthracene	208	nd	nd	nd
Total[d]	91,200	66,320	68,200	60,640

[a] Using waste 14.

[b] Centrifuged in open 250-mL glass bottles, 400 times gravity for 1 h.

[c] nd = not detected.

[d] Total = all elutable compounds using GC.

collected from the column and isolated using a solvent partition technique (Table 4.24, ca. 60,000 to 90,000 µg/100 g), suggests that the in-line XAD-2 resin cartridge (16.8 mL) may not be the most effective means of collecting organic compounds. For example, for the waste tested (No. 14) approximately three to four times more elutable compounds were detected using the solvent partition method to isolate and concentrate organic compounds from the aqueous effluent. The treatment of the internal standard (azulene) was different for these two extracts (in the case of the column/XAD-2 system, the internal standard was added after resin extraction; with the solvent extraction system the azulene was added to the aqueous phase prior to extraction). However, in view of the high recoveries (> 75%) normally obtained for azulene, it is unlikely that the large differences in organic chemical levels noted between the two isolation techniques can be attributed to differences in the handling of the internal standard.

Amounts of organic compounds observed among the batch extracts after the four separation treatments can be found in Table 4.25. Phenanthrene was again not detected in any of the extracts filtered through the Millipore filters. It is interesting to note that benzo(a)anthracene was not found in any of the batch extracts, regardless of the filter type used, while it was observed in the glass-fiber-filtered column extract (see Table 4.24). In all cases, where extracts were filtered through glass fiber filters, the column extract contained greater quantities of organic compounds than did the extracts from the batch procedures.

TABLE 4.25. ORGANIC COMPOUNDS REMAINING IN A BATCH WATER EXTRACT AFTER USING FOUR SOLID/LIQUID SEPARATION TREATMENTS[a]

	Filtered			
Compound	Glass fiber (0.7-μm)	Nuclepore (0.4-μm)	Millipore (0.45-μm)	Centrifuged[b]
	- - - - - - - - - -	μg/100 g waste	- - - - - - - - - -	
o-cresol	3056	4380	3376	3856
Naphthalene	4564	3032	4784	4520
Quinoline	100	100	108	104
Naphthol	96	80	60	132
Dibenzothiophene	60	48	36	64
Phenanthrene	168	60	nd	168
Carbazole	64	56	48	64
Benzo(a)anthracene	nd	nd	nd	nd
Total[d]	43,240	45,280	46,000	44,400

[a] Using waste 14.

[b] Centrifuged in open 250-mL glass bottles, 400 times gravity for 1 h.

[c] nd = not detected.

[d] Total = all elutable compounds using GC.

When a standard solution containing known concentrations of selected organic compounds was subjected to the different solid/liquid separation treatments, differing amounts of organic compounds were also found (Table 4.26). In general, the glass fiber filter exhibited lower sorption properties. Again, certain organic compounds [dibenzothiophene, phenanthrene, and benzo(a)pyrene] were not found in the Millipore-filtered sample from any extract (<1 µg/L). Additional losses of organic compounds were seen when the standard solution was agitated for 24 h (Table 4.27). This loss is probably due to sorption of the compounds on the glass container walls. This may also explain the loss of organics in the centrifuged samples (i.e., samples were centrifuged in glass bottles). Volatilization may also have occurred in the centrifuged samples.

4.2 Task 2: Comparison of Two Sample Preparation Protocols for Performing the Ames Test on Solid Waste Extracts and Wastewaters

The results of the recovery study comparing isolation of two organic compounds [benzo(a)pyrene (BaP) and 9-amino-acridine] from extracts and wastewaters using the XAD resin adsorption and solvent partition techniques are shown in Table 4.28. The BaP recovery values are somewhat confounded by the fact that the added BaP was well in excess of its water solubility (1 mg/L added relative to a water solubility of below 10 µg/L). Thus, the recovery data for solvent partition showed an unexpected distribution of BAP into the acid fraction, implying that three extractions with methylene chloride were not sufficient to remove all of the BAP into the base/neutral

TABLE 4.26. ORGANIC COMPOUNDS REMAINING IN A STANDARD SOLUTION AFTER USING FOUR TREATMENTS FOR SEPARATING SOLID AND LIQUID PHASES[a]

Compound	Filtered			
	Glass fiber (0.7-μm)	Nuclepore (0.4-μm)	Millipore (0.45-μm)	Centrifuged[b]
	mg/L			
Phenol	7.8	7.8	7.7	6.0
o-cresol	8.6	8.8	8.1	9.2
Naphthalene	5.8	1.3	1.0	6.1
Quinoline	6.3	6.7	5.2	7.0
Naphthol	6.6	7.7	7.0	7.9
Dibenzothiophene	9.2	9.7	nd[c]	6.7
Phenanthrene	9.7	11.5	nd	5.9
Carbazole	11.6	2.0	1.3	6.6
Fluoranthene	7.4	8.8	nd	7.8
Benzo(a)anthracene	4.4	3.8	nd	5.7

[a] Approximately 10 ppm of each compound added to prepare standard solution.

[b] Centrifuged in open 250-mL glass bottles, 400 times gravity for 1 h.

[c] nd = not detected at 1 mg/L.

TABLE 4.27. ORGANIC COMPOUNDS REMAINING IN A STANDARD SOLUTION (AGITATED FOR 24 HOURS) AFTER USING FOUR SOLID/LIQUID PHASE SEPARATION TREATMENTS[a]

Compound	Filtered Glass fiber (0.7-μm)	Filtered Nuclepore (0.4-μm)	Filtered Millipore (0.45-μm)	Centrifuged[b]
	mg/L	mg/L	mg/L	mg/L
Phenol	7.2	5.9	4.2	4.3
o-cresol	8.1	8.3	6.7	8.2
Naphthalene	5.2	2.9	3.2	3.4
Quinoline	5.3	4.9	5.4	7.4
Naphthol	6.3	7.4	5.3	8.2
Dibenzothiophene	4.6	4.3	nd[c]	4.8
Phenanthrene	4.7	4.3	nd	5.1
Carbazole	4.8	4.5	1.8	5.5
Fluoranthene	3.4	2.6	nd	4.6
Benzo(a)anthracene	2.1	1.8	nd	3.2

[a] Approximately 10 ppm of each compound added to prepared standard solution; standard solution was agitated for 24 h.

[b] Centrifuged in 250-mL glass bottles, 400 times gravity for 1 h.

[c] nd = not detected at 1 mg/L.

TABLE 4.28. COMPARISON OF TWO ISOLATION TECHNIQUES FOR REMOVING ORGANIC MUTAGENS FROM WASTEWATERS AND SOLID WASTE EXTRACTS

	% recovery[a]					
	XAD-2 resin			Solvent partition		
Aqueous medium	Base/ neutral	Acid	Total	Base/ neutral	Acid	Total
	- - - - - - - - Benzo(a)pyrene[b] - - - - - - - -					
Water	77.0	1.5	78.5	50.0	22.0	72.0
EP[c]	87.5	3.0	90.5	55.5	24.5	80.0
Leachate[d]	85.0	1.5	86.5	27.5	7.5	35.0
Wastewater[e]	83.0	4.5	87.5	83.0	7.5	90.5
	- - - - - - - - 9-amino acridine[f] - - - - - - -					
Water	78.0	0.0	78.0	93.5	0.0	93.5
EP[c]	83.5	2.0	85.5	72.5	0.0	72.5
Leachate[d]	78.5	1.0	79.5	74.0	0.0	74.0
Wastewater[e]	85.5	0.0	85.5	96.5	0.0	96.5

[a] 1 mg/L of mutagen added, average of two replicates.

[b] Recovery measured using both HPLC and scintillation counting (results agreed ± 2%).

[c] Solid waste extract using the EPA-EP with waste 10.

[d] A waste leachate collected at a landfill containing waste 3.

[e] Coal conversion wastewater.

[f] Recovery measured using fluorescence spectrophotometry.

fraction. However, for the soluble 9-amino-acridine, the recovery distribution was excellent.

Using Duncan's multiple range test, the only significant difference ($P < 0.05$) in recovery of the BaP or 9-amino-acridine between the two isolation techniques was noted with BaP in landfill leachate. Significant precipitation and subsequent emulsion formation took place using the solvent partition technique, which could account for the difference noted. There were also some significant differences ($P < 0.05$) in the recovery of BaP and 9-amino-acridine by the solvent partition technique, depending on the type of aqueous medium spiked with these chemicals. For example, in addition to the very low recovery of BaP in the landfill leachate (35%), the recovery of BaP from the water and EP extract (72 and 80% recovery, respectively) was significantly lower than its recovery by solvent partition from coal conversion wastewater (90.5% recovery). The nature of the aqueous medium also affected the recovery of 9-amino-acridine. In this case, the recovery from the EP extract and landfill leachate (72.5 and 74.0%, respectively) was significantly ($P < 0.05$) lower than that recovered from the water or coal conversion wastewater (93.5 and 96.5%, respectively). In contrast, there were no observed differences in the recovery of either BaP (range 77.0% to 90.5%) or 9-amino-acridine (78.0% to 85.5%) among the aqueous media using the XAD-2 resin technique. These data suggest that the XAD-2 resin technique is preferable to solvent partition if a wide range of aqueous media are to be investigated.

Mutagenicity testing results of the positive controls and the organic isolates from the recovery study are shown in Tables 4.29 to 4.31. The mutagenic activity was directly related to the chemical distribution of benzo(a)pyrene and 9-amino-acridine. There was no indication of interference from other organic species present in the extracts.

Aqueous media spiked with 9-amino-acridine were directly mutagenic when tested with TA1537. When assayed with metabolic activation applied, activity was also seen with TA1538, TA98, and TA100.

The benzo(a)pyrene-spiked extracts showed no mutagenic activity with any strain in the absence of metabolic activation. Strong positive responses were observed in TA1537, TA1538, TA98, and TA100 when metabolic activation was applied. Qualitatively, the mutagenic activity of the spiked extracts was identical to the results obtained with the positive control samples of 9-amino acridine and benzo(a)pyrene.

In summary, there was no major difference in the ability of the two techniques to recover BaP or 9-amino-acridine from wastewaters. The single observed difference was the very poor recovery of BaP in the landfill leachate by the solvent partition technique (35% recovery compared to 86.5% recovery by XAD-2). However, in the solvent partition technique, recovery appeared to be dependent on the aqueous medium. Recovery by the XAD-2 technique, on the other hand, was observed to be independent of the aqueous matrix. Furthermore, the resin isolation procedure (XAD-2 resin) is superior, from a practical standpoint, for the following reasons:

TABLE 4.29. MUTAGENIC ACTIVITY OF THE POSITIVE CONTROLS BENZO(A)PYRENE AND 9-AMINO ACRIDINE

Compound	Strain				
	TA1535	TA1537	TA1538	TA98	TA100
	- - - - - - Revertants/μL - - - - - -				
Benzo(a)pyrene (25 ng/μL)					
With activation	0	9.5	13.1	7.4	4.2
Without activation	0	0	0	0	0
9-amino acridine (25 ng/μL)					
With activation	0	1.4	2.0	1.7	0.9
Without activation	0	3.1	0	0	0

TABLE 4.30. MUTAGENIC ACTIVITY IN ORGANIC ISOLATES: COMPARISON OF RECOVERY TECHNIQUES USING BENZO(A)PYRENE

	Revertants/μL[a]			
	Resin		Solvent partition	
Aqueous medium	Base/neutral	Acid	Base/neutral	Acid
	TA1537, Aroclor activation			
Water	7.0	0	4.0	0.3[b]
EP	8.1	0	5.6	1.2
Leachate	6.9	0	4.7	1.4
Wastewater	7.4	0	4.4	1.3
	TA1538, Aroclor activation			
Water	11.5	0	4.5	3.8[b]
EP	11.5	0	5.4	3.0
Leachate	10.2	0	4.6	2.6
Wastewater	11.2	0	4.7	2.2
	TA98, Aroclor activation			
Water	8.0	0	5.4	1.5[b]
EP	8.7	0	6.4	1.9
Leachate	8.1	0	6.9	2.6
Wastewater	8.9	0	7.3	2.4
	TA100, Aroclor activation			
Water	5.7	0	3.8	0.8[b]
EP	4.6	0	2.9	1.8
Leachate	8.2	0	5.0	2.1
Wastewater	3.8	0	3.5	1.6

[a] Average of two replicates.

[b] Single determination.

TABLE 4.31. MUTAGENIC ACTIVITY IN ORGANIC ISOLATES: COMPARISON OF RECOVERY TECHNIQUES USING 9-AMINO ACRIDINE

Aqueous medium	Revertants/μL[a]			
	Resin		Solvent partition	
	Base/neutral	Acid	Base/neutral	Acid
	TA1537, No activation			
Water	1.7	0	2.4	0
EP	2.2	0	2.4	0
Leachate	2.7	0	2.1	0
Wastewater	1.6	0	2.2	0
	TA1538, Aroclor activation			
Water	0.7	0	0.9	0
EP	0.8	0	1.2	0
Leachate	1.3	0	1.1	0[b]
Wastewater	1.1	0	0.8	0
	TA98, Aroclor activation			
Water	0.8	0	1.7	0
EP	0.9	0	0.5	0
Leachate	1.4	0	1.0	0[b]
Wastewater	1.2	0	0.9	0
	TA100, Aroclor activation			
Water	1.0	0	1.4	0
EP	1.3	0	0.6	0
Leachate	1.2	0	1.7	0
Wastewater	0.9	0	0.9	0

[a] Average of two replicates.

[b] Single determination.

(1) It is technically simpler, and a series of XAD columns can be used to facilitate handling large numbers of samples.

(2) There are no problems with emulsion formation. Emulsions may pose severe problems in solvent partition techniques with "dirty" water samples, e.g. the real-world landfill leachate.

(3) It is more economical; much less solvent is consumed.

However, the resin procedure has limitations. If significant precipitation occurs during pH adjustment, flow of water through the column can be impeded, increasing extraction time. Also batch-to-batch variability in the resin, as well as contamination, requires that extensive clean-up of the resin is necessary to ensure reproducibility.

4.3 Task 3: An Evaluation of the Equivalence of Magnetically Stirred Extractor Relative to an EPA-Approved Rotary Extractor for Conducting the EP

A magnetically stirred extractor and a rotary extractor were compared for conducting the EP. Using the low frequency tachometer (see Section 3.2.5), the stirring rates for the magnetically stirred extractor were recorded every hour during the 24-h extraction for wastes 12 and 13. Figures 4.10 and 4.11 present the mean speed and the standard deviation found for the four replicate EP extractions during the extraction period. Waste 12 was a very hard granular solid, and 427 rpm represented the lowest mean rate (over the 24 h) required to keep the solids suspended. Waste 13 was a powdery solid, high in magnetite, which was expected to load the magnetic stirrer. Even so, a lower mean 24-h stirring rate of 342 rpm was obtained. In both cases, the stirring speed gradually increased for 1 to 2 h after adding the solids to the extractor. The stirring rate was reproducible between

ORNL-DWG 81-21532 ESD

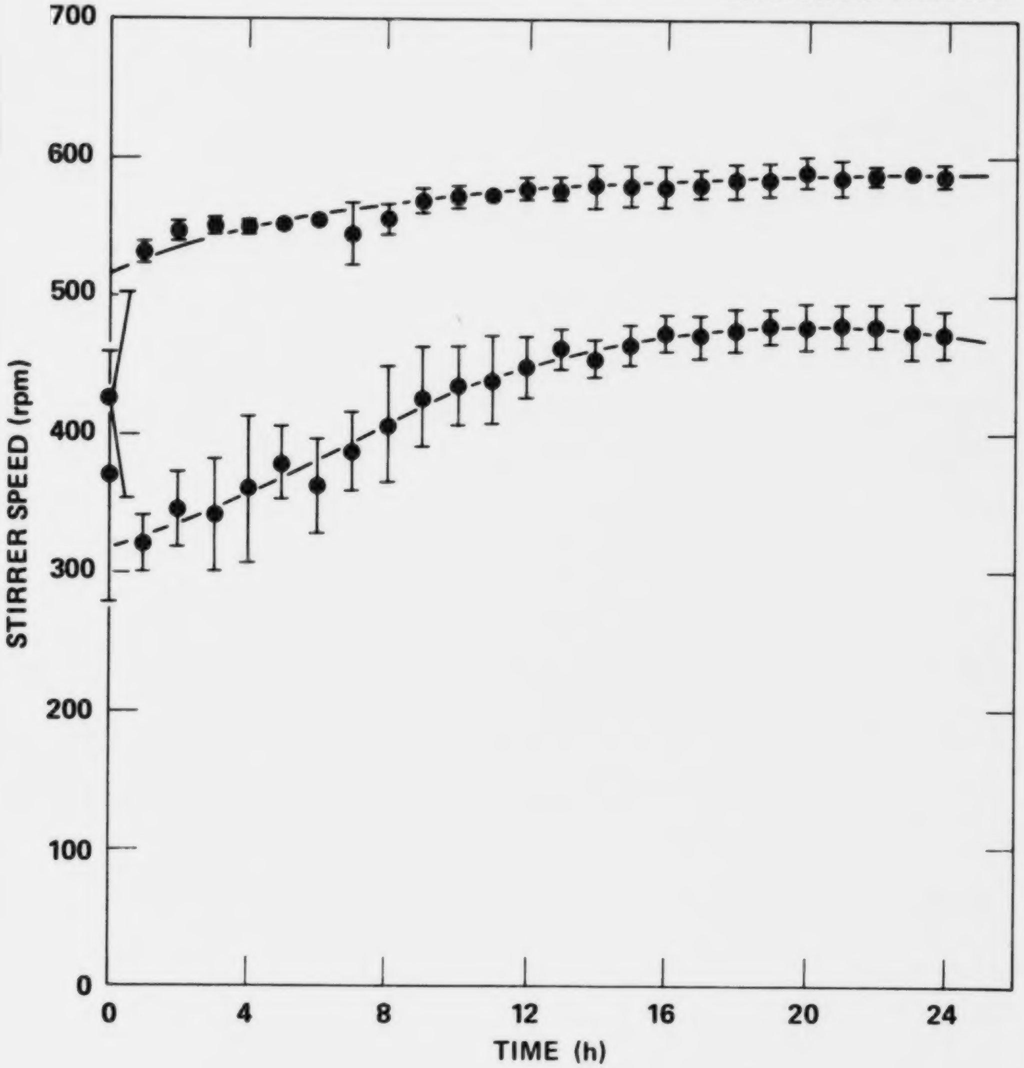

Fig. 4.10. High and low stirrer speed values for waste 12 - mean and standard deviation values for four replicate extractions over the 24-h extraction time.

ORNL-DWG 81-21533 ESD

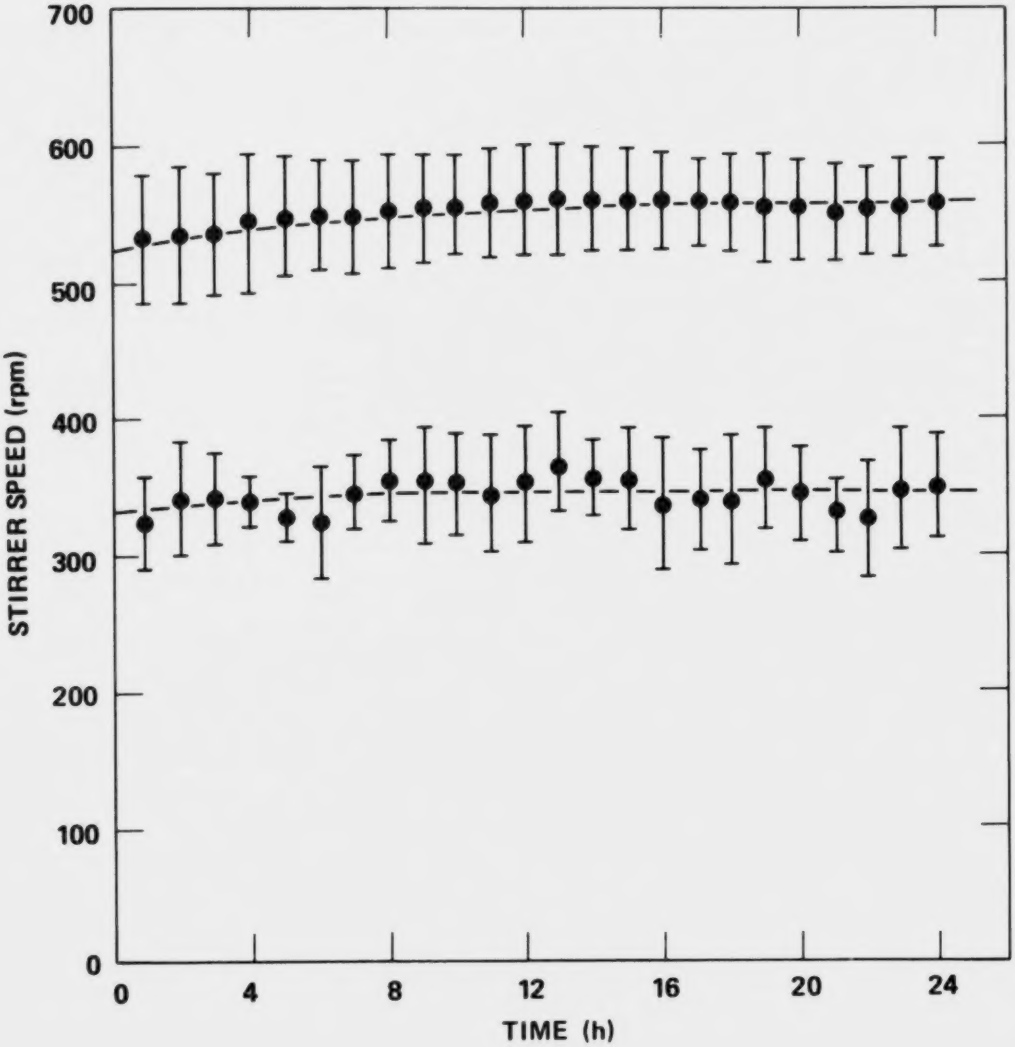

Fig. 4.11. High and low stirrer speed values for waste 13 - mean and standard deviation values for four replicate extractions over the 24-h extraction time.

the four replicate runs of each 24-h extraction; for example, the coefficients of variation (calculated each hour for the four extractions) for wastes 12 and 13 were 6 and 3% for the highest speed and 12 and 5% for the lowest speed, respectively.

The percent variation associated with the variables of agitation method, replicate extractions, and analytical procedure was determined using variance component analysis (Table 4.32). The major source of variation was associated with the agitation method (39-95%), although the amount differed depending on the waste and element. The amount of variation associated with extraction replicates and analytical procedure also differed according to waste and element, ranging from 5.0 to 39.1% for extraction replicates and 0.3 to 22.0% for analytical procedure.

Mean inorganic concentrations for wastes 12 and 13 and statistical differences found between agitation methods are shown in Table 4.33. In all cases, the magnetic stirrer agitation method produced statistically ($P < 0.05$) different inorganic concentrations than the rotary extractor. Neither method showed consistently higher concentrations. For waste 12, the rotary extraction method extracted greater amounts of Cd, while Fe and Ni concentrations were higher using the magnetic stirrer at either stirring rate. For waste 13, concentrations of As were highest using the rotary extractor; Cd concentrations were highest using the magnetic stirrer, and Zn values were lowest using the high-speed magnetic stirrer. It is interesting to note that concentrations of a more volatile element such as As are considerably reduced when using the open magnetic stirrer system versus

TABLE 4.32. DISTRIBUTION OF VARIATION ASSOCIATED WITH THE VARIABLES OF AGITATION METHOD, REPLICATE EXTRACTION, AND ANALYTICAL PROCEDURE[a]

Sample	Variable	Element		
		- - - - - - - - % - - - - - - -		
		Cd	Fe	Ni
12	Agitation method	38.9	78.7	71.9
	Agitation replicates	39.1	17.1	10.9
	Analytical procedure	22.0	4.2	17.2
		As	Cd	Zn
13	Agitation method	94.7	59.4	71.9
	Agitation replicates	5.0	26.7	6.0
	Analytical procedure	0.3	13.9	22.1

[a] Determined using variance component analysis (SAS Institute, Inc., 1979).

TABLE 4.33. MEAN ($\bar{x}$) CONCENTRATIONS AND STATISTICAL DIFFERENCES OF SELECTED INORGANIC COMPOUNDS USING A MAGNETIC STIRRER (2 AGITATION RATES) AND A ROTARY EXTRACTOR[a]

Waste	Agitation	Element		
		- - - - - -	µg/L	- - - - - -
		Cd	Fe	Ni
12	Magnetic stirrer - high speed	66^*	36^+	2077^+
	Magnetic stirrer - low speed	70^+	47	2042^+
	Rotary extractor	76	22^*	1777^*
		As	Cd	Zn
13	Magnetic stirrer - high speed	99^*	91^+	564^*
	Magnetic stirrer - low speed	343^+	91^+	1084
	Rotary extractor	548	78^*	880^+

[a] Values within a sample for a particular element that have different superscripts are significantly different ($P < 0.05$), as determined using Duncan's multiple range test (SAS Institute, Inc., 1979).

the closed rotary system. This is also supported by the fact that high-speed stirring produced lower As concentrations than did the slower stirring speed. Concentrations of the other elements investigated also differed between the high- and low-speed stirring rates; where statistical differences were found (for Cd, Fe, Zn), the high-speed magnetic stirrer yielded lower amounts.

In summary, differences can be expected in inorganic contaminant concentrations when using a magnetic stirrer extractor versus rotary extractor. Neither method will yield consistently higher concentrations than the other. However, because the concentrations of elements in these samples were very low (ppb-range), it is recommended that additional samples containing higher levels of extractable constituents be studied. If volatile constituents are of interest, the closed rotary extractor may be the preferred method, although this system does not allow for automatic pH adjustment.

4.4 Task 4: An Evaluation of the Reverse-Phase High-Pressure Liquid Chromatography (HPLC) Protocol for Assessing the Bioaccumulation Potential of Solid Waste Extracts

Nine wastes were tested for bioaccumulative materials using the bioaccumulation potential test as described in Section 3.3.4. The materials tested were the organic isolates from the Soxhlet and sequential extraction fractions, and the organic concentrates from the five aqueous extraction procedures on the nine wastes. Table 4.34 illustrates data collected in terms of the number of chromatographic peaks found with retention times equal to or greater than log P = 3.0 as well as the total peak area with respect to bromobenzene. All wastes, with the exception of wastes 1 and 3 were found to contain

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TABLE 4.34. BIOACCUMULATION DATA ON SOLID WASTE ISOLATES: AQUEOUS EXTRACTS AND ORGANIC ISOLATES[a]

		Aqueous extracts				Organic isolates			
							Sequential extraction		
Waste	EP	Water	Na-resin	Citrate buffer	Column	Soxhlet	Acid	Base	Neutral (x10)
	Number of peaks[a]/Total area[b]								
1	0	0	0	0	2/2.61	0	0	0	nd[c]
2	0	0	0	0	14/14.7	0	0	0	1/2.0
3	0	0	0	0	12/185	0	0	0	16/235
4	0	0	0	0	16/10.4	0	1/17.5	0	1/31.0
5	0	0	0	0	17/47.8	0	2/30.6	1/17.3	1/4.21
6	0	0	0	0	13/98.6	3/22.6	3/44.7	0	3/93.1
7	ne[d]	0	0	ne	ne	7/214.4	0	0	4/39.5
8	0	0	3/12.3	1/1.79	ne	9/837.9	0	0	8/1757.1
9	0	0	0	0	9/5.8	6/49.5	3/12.8	1/3.9	5/247.8

[a] No. of peaks above log P = 3.

[b] %, compared to standard bromobenzene.

[c] nd = not determined.

[d] ne = not extended.

bioaccumulative materials, as identified in the Soxhlet isolates and sequential extraction fractions, but none of these materials were observed in the organic concentrates from the aqueous batch extraction tests. An exception was waste 8 which contained by far the highest levels of these components. The low quantities of bioaccumulative compounds observed in the batch extracts are probably due in large measure to the low water solubility of the bioaccumulative compounds which promotes their loss by adsorption on the membrane filters utilized in the batch extractions.

Considering the highly lipiphilic nature of bioaccumulative materials, it is interesting to note that significant levels of these materials were isolated in the column extracts. In almost all cases, the materials found to be bioaccumulative in the solid wastes (by Soxhlet and sequential extraction) were also found in the column extracts. Among the aqueous extraction procedures, only the column procedure is effective for the detection of bioaccumulative materials, using the current methodology.

The bioaccumulation potential test itself has several drawbacks. No UV detector is not universal (therefore, nonabsorbing materials such as chlorinated aliphatic compounds may be missed) nor is the response of the UV detector uniform (highly absorbing materials may be given too high a ranking). Therefore, information obtained is essentially qualitative. However, the test does provide a useful screening method for the detection of potential bioaccumulative organic compounds in the wastes as well as in the extracts.

SECTION 5. CONCLUSIONS

5.1 Task 1: An Evaluation of Extraction Procedures to Remove Nonpolar Organic Compounds from Solid Wastes

The primary objective of Task 1 was to assess the capabilities of five selected extraction procedures to remove organic compounds from 11 solid wastes. Other objectives included mutagenicity testing of the extracts and examining the solid wastes for organic compounds (Soxhlet and sequential extraction) and the solid waste extracts for selected inorganic constituents. The five extraction procedures used were four batch extractions and an upward flow column extraction. The following extracting media were used:

(1) Batch 1: EP, acetic acid, pH 5.0,

(2) Batch 2: deionized distilled water,

(3) Batch 3: deionized distilled water with a sodium displacement resin, and

(4) Batch 4: 0.5 M citrate buffer,

(5) Column: deionized distilled water.

The following conclusions are based on data presented for Task 1:

- For the four batch extractions, the citrate buffer extracts consistently showed highest concentrations of inorganic compounds.
- Of the two methods compared for identification of organics in the waste samples (Soxhlet extraction with methylene chloride and a three-step sequential extraction procedure developed at ORNL), the three-step sequential extraction scheme consistently extracted more organic material than did the Soxhlet extraction.

- No significant differences in organic concentrations (based on DOC levels) were found between water and Na-resin extracts.
- No significant differences were found in DOC values between glass fiber and Nuclepore-filtered extracts from the water and Na-resin extracts.
- Total chromatographable organic (TCO) content data for the five extraction procedures revealed that the column procedure extracted more organic material than did any of the batch extraction procedures.
- When the five extraction procedures were ranked from lowest to highest (1 to 5) for the ability to extract total chromatographable organics (TCO), the column procedure produced extracts higher in TCO and selected organic compounds than batch extracts ($P < 0.05$).
- Of the four batch extraction procedures, the water procedure extracted the highest levels of TCO and selected organic compounds ($P < 0.05$).
- No significant differences in the ability to extract organic compounds were observed among the EP, Na-resin, citrate buffer extractions.
- In general, the column leaching procedure was the most aggressive means of extracting organic compounds from solid wastes. The most noticeable differences between the column procedure and the batch procedures were the levels of moderately volatile compounds and the nonpolar compounds found in the extracts.

- The five extraction procedure extracts, as well as the Soxhlet solid waste isolate and the solid waste isolates produced from the sequential procedure, were compatible with the *Salmonella*/microsome assay.
- Of the nine wastes examined, seven yielded organic isolates that possessed detectable mutagenic activity. The *Salmonella*/microsome mutagenicity assay performance comparison with the nine wastes indicated that, of the five aqueous extraction procedures, the Na-resin extraction was the most effective extraction, revealing four of the mutagenic activities detected.
- Six mutagenic waste components were identified (from five wastes) by the sequential extraction method. This method has the great advantage of (1) indicating the class fractions harboring the active components and (2) revealing multiple mutagenic components.
- Only one of the nine EP extracts examined exhibited mutagenic activity.
- The coefficient of variation associated with replicating the column extraction procedure was 13%.
- The use of glass fiber filters for the separation of solid and aqueous phases allows higher recovery of organic compounds than filtering with Nuclepore and Millipore filters.
- For a single waste, the column extraction procedure extracted greater quantities of total chromatographable organic compounds than a closed batch extraction, even when the extracts were filtered through the same filter type.

5.2 Task 2: Comparison of Two Sample Preparation Protocols for Performing the Ames Test on Solid Waste Extracts and Wastewaters

The objective of Task 2 was to compare two techniques for the isolation of organic mutagens for performing the Ames test on solid waste extracts and wastewaters. The two recovery techniques were a resin absorption technique using Amberlite XAD-2 resin and a solvent partition technique using methylene chloride. Two mutagens were examined, benzo(a)pyrene and 9-amino acridine. The following was concluded:

- There were no major differences in the ability of the two techniques to recover BaP or 9-amino acridine from wastewater.
- One exception was the very poor recovery of BaP in the landfill leachate by the solvent partition technique.
- The recovery of BaP and 9-amino acridine was dependent on the aqueous matrix using the solvent partition technique.
- Recovery of the mutagens by the XAD-2 technique was independent of the aqueous matrix.
- The various aqueous matrices employed did not appear to modify the amount of mutagenic activity attributable to benzo(a)pyrene and 9-amino acridine.
- From a laboratory performance standpoint, the resin isolation procedure was considered superior.
- The resin procedure, has its limitations. If significant precipitation occurs during pH adjustment, flow of water through the column XAD-2 cartridge can be impeded.

5.3 Task 3: An Evaluation of the Equivalence of a Magnetically Stirred Extractor Relative to an EPA-Approved Rotary Extractor for Conducting the EP

The objective of Task 3 was to compare a magnetically stirred extractor with an EPA-approved rotary extractor for conducting the EP. The conclusions were as follows:

- The high and low stirring rates obtained using the magnetically stirred extractor between replicate extractions of two wastes showed low variability. Coefficient of variation values for the two wastes were 6 and 3% for the high speed and 12 and 5% for the low speed.
- The percent variation (determined using variance component analysis) associated with the variables of agitation method, replicate extractions, and analytical analysis differed depending on the waste and metal. The major source of variation, however, was associated with the agitation method, ranging from 39 to 95%.
- The magnetic stirrer agitation method produced statistically different inorganic concentrations than the rotary extractor. Neither method showed consistently higher concentrations.
- If volatile constituents are of interest, the sealed rotary extractor is the preferred method, although this system does not allow for automatic pH adjustment.

5.4 Task 4: Evaluation of the Proposed Reverse-Phase High-Pressure Liquid Chromatography (HPLC) Protocol for Assessing Bioaccumulation Potential of Solid Waste Extracts

The objective of Task 4 was to evaluate the proposed reverse-phase High-Pressure Liquid Chromatography (HPLC) protocol (EPA 1978) to assess the bioaccumulation potential of solid waste extracts. Soxhlet extracts, acid/base/neutral fractions from the sequential extraction procedure, and the organic isolates from the aqueous extracts of the five extraction procedures produced in Task 1 were tested for bioaccumulative material. The following was concluded:

- Of the five aqueous extraction procedures, only the column extraction produced extracts that contained bioaccumulative material.
- A majority of the Soxhlet isolates and sequential extraction procedure fractions of the solid wastes contained bioaccumulative organics.
- The bioaccumulation test itself has several drawbacks; the UV detector is not universal (therefore, nonabsorbing materials may be missed) and the response of the UV detector is not uniform.
- The present bioaccumulation protocol can provide a screening method for the detection of potentially bioaccumulative organic compounds in the wastes as well as in their leachates.

SECTION 6. FUTURE RESEARCH

Further research should be conducted to determine if the up-flow column extraction procedure is superior to batch-mode extractions for a variety of wastes and extracting media. It appears that one of the major faults in the batch-mode extractions is the filtration step: (1) it is very time consuming for some samples, and (2) the filtration using 0.40- to 0.45-µm membrane filters appears to sorb significant quantities of certain organic compounds. It was demonstrated that up-flow column extracts not filtered through membrane filters contained significantly greater quantities of total chromatographable organic compounds than batch extractions which were filtered through 0.4-µm pore size filters. When water was used as the common extracting medium for a single waste in both the up-flow column and a batch-mode extraction, the total quantity of elutable organic compounds by gas chromatography was 1.4 to 2.1 times higher using the up-flow column. The quantity of organic compounds varied according to the method of liquid/solid phase separation and type of filter. Further experiments should be conducted to confirm if this is typical for a variety of wastes and possibly for different classes of extracting media.

Regardless of which type of extraction procedure is found to be superior for extracting organic compounds (either up-flow column or batch extraction), its relevance to simulating the leaching of organic and inorganic constituents from wastes co-disposed in a municipal landfill environment needs to be established. The present EP was conceived as a first-order approximation to simulate leaching action of the low molecular weight carboxylic acids generated in an actively decomposing municipal landfill. It uses acetic acid, the carboxylic acid most prevalent in municipal waste landfill leachate. The acetic acid, because of its weak acidic character, plays a dominant role in the leaching of metals; however, its role relative to the removal of polar and nonpolar organic compounds from wastes is unclear. Acetic acid also was not compatible with a variety of biotesting procedures (Epler et al. 1980). Thus, the limitations of acetic acid as an extracting medium were the impetus behind this past year's research.

Future research needs to (1) confirm the aggressiveness of the up-flow column to remove organic and inorganic constituents from a variety of wastes using selected leaching media, and (2) test the effectiveness of the up-flow and batch-mode extractions to simulate leaching by municipal waste leachate. The objective of this research is to develop a second generation test for mobility, henceforth known as EP-III, that will more accurately and reproducibly model leachate production, for inorganic as well as organic constituents, in a co-disposal municipal landfill. A workplan with these objectives is appended (Appendix B).

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APPENDIX A

QUALITY ASSURANCE PROJECT PLAN

For

"Toxicity of Leachates Project"

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Revision No. 1

April 15, 1982

Interagency Agreements
DOE 40-1087-80
USEPA AD-89-F-1-058

APPROVAL:

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1. Project Description

The objective of the research is to develop a laboratory extraction test for solid wastes that: (1) models the leaching action a waste would undergo when disposed of, along with a municipal waste, in a municipal waste landfill following a 95/5 (weight fraction of municipal and industrial waste) co-disposal scenario, (2) is compatible in aquatic toxicity and phytotoxicity testing protocol, and (3) is relatively inexpensive to conduct in terms of time, equipment, and personnel. The extraction test will be henceforth referred to as EP-III.

The project involves research in both the laboratory and field. The laboratory work is centered on evaluating the extraction conditions that are most aggressive in removing inorganic and organic constituents from four selected industrial wastes by a particular municipal waste leachate (MWL). Municipal waste leachate has been obtained from a lysimeter located at the U.S. Army Corps of Engineers Waterways Experiment Station (WES), Vicksburg, Mississippi, for this work. The extraction procedure (column aerobic, column anaerobic, or rotary batch) found to be most aggressive will serve as baseline data to be simulated by the laboratory method developed for EP-III. The laboratory variables to be investigated in this phase of the work will consist of the type of extraction procedure (up-flow column or batch rotary) and type of extraction media (acetate buffer, CO_2-saturated water, distilled water, or synthetic leachate). The experiment will consist of a factorial arrangement of 11 treatments and four industrial wastes in a randomized block design with two blocks (time) per treatment-waste combination. The 11 treatments will consist of the eight (procedure x media) laboratory methods plus the three WES/MWL extractions.

The field work will test the ability of various laboratory extraction methods to simulate the leaching characteristics of industrial wastes in large-scale field lysimeter experiments containing wastes in a 95% municipal to 5% industrial scenario and will evaluate the aggressiveness relative to age of a municipal waste leachate to extract contaminants from industrial wastes.

Municipal waste leachate from two large-scale lysimeters (1.8 m in diameter and 3.6 m in height) will be diverted to 16 columns per lysimeter containing four industrial wastes (the same wastes used in the laboratory studies). For each lysimeter, one-half of the columns (4 wastes x 2 replicates) will be used to compare the 95% municipal and 5% industrial waste scenario to the laboratory extraction studies. The remaining columns will be used to evaluate the relative aggressiveness of the municipal waste leachate as a function of age of the leachate. The projected work schedule is presented in Table 1.

TABLE 1. PROJECTED WORK SCHEDULE

Milestone	Projected Date
1. Laboratory study	
WES municipal leachate procured	Jan. 27, 1982
Industrial wastes (8) procured	May 15, 1982
Proximate analysis of wastes initiated	May 15, 1982
Select sastes (4) for laboratory and field studies	May 31, 1982
Laboratory extractions started (88 extractions)	June 1, 1982
Laboratory extractions completed	Sept. 1, 1982
Inorganic and organic analysis of extracts completed	Sept. 15, 1982
Statistical analyses completed	Oct. 15, 1982
2. Field Study	
Municipal refuse obtained and lysimeters packed	Feb. 23, 1982
Industrial waste columns packed for laboratory Comparison and aggressiveness of MWL, begin leaching	June 15, 1982
Laboratory comparison, leaching completed	Aug. 10, 1982
Inorganic and organic analyses of leachates from laboratory comparison completed	Sept. 1, 1982
Aggressiveness of MWL, leaching completed	Sept. 15, 1982
Inorganic and organic analyses of leachates from aggressiveness of MWL completed	Oct. 1, 1982
Statisical analyses completed, aggressiveness of MWL	Oct. 15, 1982
3. Draft report on laboratory and field studies	Jan. 1, 1983

2. Project Organization and Responsibility

The project directly involves personnel from two Divisions at Oak Ridge National Laboratory (ORNL): (1) the Environmental Sciences Division (ESD) and (2) the Analytical Chemistry Division (ACD). The Environmental Sciences Division is responsible for conducting the solid waste extractions, developing experimental design, performing statistical analysis, and interpretating environmentally related data. The Analytical Chemistry Division is responsible for inorganic and organic analyses of the leachates and extracts. The project is managed from the Environmental Sciences Division (Fig. A-1).

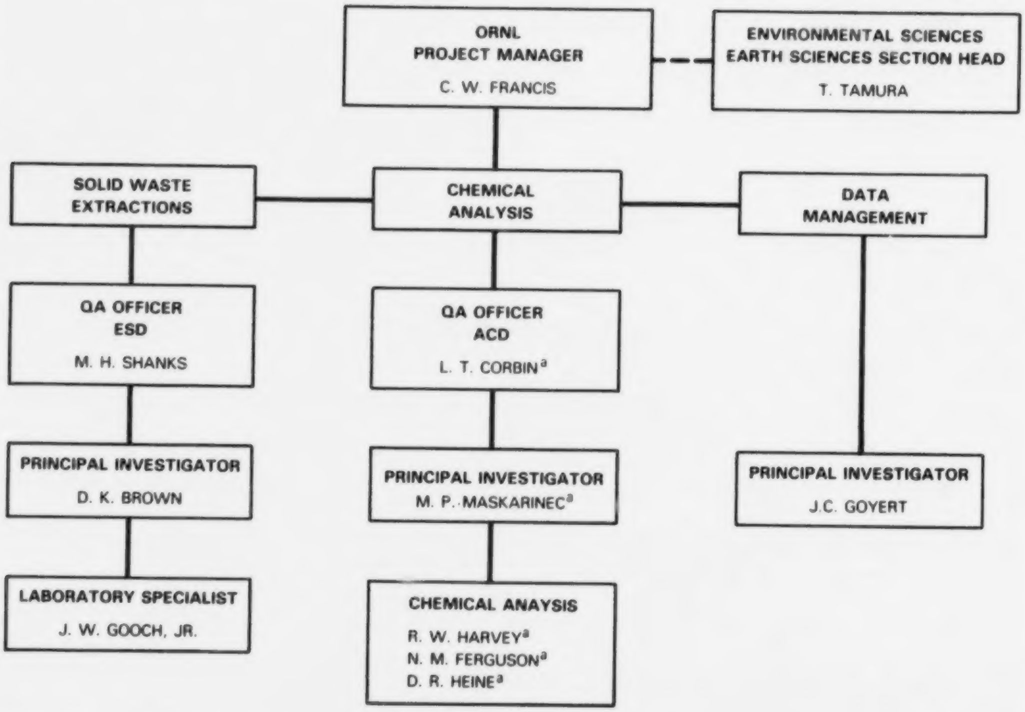
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Fig. A-1. Project organization and responsibilities.

3. QA Objectives in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

3.1 Organic Analyses

Standard methods are in place for the classes of organic compounds expected to occur in the solid waste extracts: PAH's, phenols, purgeable halocarbons, and aliphatic hydrocarbons. The isolation of the organic compounds is performed according to EPA methods 624 and 625. By using check standards (externally prepared) and periodic repetitive analyses of selected extracts as well as National Bureau of Standards (NBS) prepared samples, QA objectives for these parameters have been established as follows:

A. Precision - The relative standard deviation of repetitive measurements on a sample should not exceed that achieved in methods development/evaluation studies. This value has been determined to be ±10% for organic analyses.

B. Accuracy - The analytical data obtained from the application of each analytical method to a check standard (of different concentration than the calibration standards) should agree within ±15% of the true value defined by its gravimetric preparation. Analytical results for samples also examined by other EPA contractors should agree statistically at the 90% confidence limits.

C. Completness - At least 80% of all possible analytical measurements should meet QA objectives.

3.2 Inorganic Analyses

Elemental inorganic analyses will be conducted by atomic absorption (AA) spectroscopy (equipped with flameless graphite furnace) and Inductively Coupled Plasma (ICP) methodologies. All samples by AA will be conducted according to standard methods (USEPA 1979) except for Hg, Se, and As analyses which will be conducted as described in Section 7.4. For AA and ICP analyses the QA objectives are as follows:

A. Precision - The relative standard deviation of repetitive measurements will vary from element to element and as a function of detection (the closer to the detection limit the higher the deviation). For samples containing elements ten times the detection limit the objective is < ±15%, while for samples near the detection limit the objective is ±100%.

B. Accuracy - Using known standards furnished by EPA, the accuracy for inorganic analyses is expected to be ±15% at levels ten times the detection limit. Near the detection limit the accuracy may decrease to 100 to 200%.

C. Completeness - At least 90% of all possible analytical measurements should meet QA objectives.

4. Sampling Procedures

Municipal refuse leachate has been obtained from the Corps of Engineers Waterways Experimental Station (WES) in Vicksburg, Mississippi. The municipal refuse leachate was collected in 3.4-L Teflon®-lined cans under pressure (using helium) in a sealed glovebox with a helium atmosphere. This leachate (approximately 125 L) will be kept anaerobic and will be refrigerated at 4°C until use. Aliquots of the municipal refuse leachate will be analyzed throughout the extraction experiments to assess any changes in the chemical nature of the samples.

The industrial wastes are being obtained through EPA's Washington Headquarters, Office of Solid Waste, Todd Kimmell (coordinator). The wastes are being shipped to ORNL in 208-L (55-gal) drums. Wastes in the drums will be thoroughly mixed before subsampling for individual extractions. A universal sampling procedure will not be applicable in obtaining representative subsamples from the drums. The types of wastes range from a total liquid to slurry and dry solid. Therefore, each waste will be examined, and a specific sampling procedure will be documented. When applicable, the drum will be placed on a drum roller to obtain a thorough mixing of the waste sample. Subsample from the drums will be analyzed for physicochemical properties to ensure adequate mixing and sampling procedures.

Municipal wastes will be collected at local municipalities and sorted to desired composition for the large-scale lysimeter studies. Sampling history, conditions, and procedures will be recorded in ORNL-registered laboratory notebooks.

5. Samples Custody

The bulk industrial wastes [208-L (55-gal) drums] and municipal refuse leachate will be stored in a locked, refrigerated cargo trailer (ORNL Bldg. 7038). The trailer is located in a locked fenced area; only authorized personnel are allowed access. The trailer was purchased and is operated for the EPA Synfuels Repository Project (DOE Activity No. 40-740-78). It is maintained at a constant 4°C temperature. The air temperature is continually recorded in the trailer with the recorder paper being changed monthly; the chart papers are kept in a permanent file by W. Griest (ACD).

All wastes, leachates, laboratory-derived extracts, extraction procedures used to obtain extracts, and important laboratory variables will be identified by a unique six-digit sample identifier code. For example, sample code 1CIN21 may represent: reconnaissance study using oil-reclaiming clay extracted aerobically in a column extraction - extraction replicate 2 and aliquot 1 analytical analysis. All persons involved with the experiments will use the same identifier code for a particular sample. The sample identifier code will be established by D. K. Brown who is in charge of the repository of waste samples. D. K. Brown also initiates sample extractions. All sample information will be logged into the data management system using the Project Results Tracking System (PRTS) (Strand et al. 1981; and Strand et al., in review). Information will be kept concerning sample delivery, dates of extraction, dates for submission for analytical analyses, completion dates of the analyses, and results of analyses. The PRTS is a complete record-keeping system that allows information to be obtained concerning the status of the project; the system also allows statistical analyses of the data without any data transferring (see Section 8).

In addition, a registered ORNL technical notebook will be kept for the solid wastes and leachate samples. A record will be kept as subsamples are taken from the storage area in terms of what samples were taken and by whom, quantities removed, and for what purpose.

In terms of waste disposal, separate labeled containers will be kept for liquid (extracts, washwater contacting solids, etc.) and solid (spent wastes, filters, etc.) wastes. Wastes will be handled and disposed of according to ORNL's Environmental Protection Manual and Hazardous Materials: Management and Control. These manuals are in-house reference manuals that are updated as needed by ORNL's Department of Environmental Management (T. W. Oakes, Department Head). Waste disposal will be handled upon advice by each Division's Environmental Protection Officer.

6. Calibration Procedures and Frequency

Each analytical instrument will be recalibrated by the operating Analytical Chemistry personnel before samples are analyzed. Flame atomic absorption will be checked after analysis of six samples. Standard addition techniques will be used for graphite furnace analysis. Commercial standards prepared for atomic absorption analysis by Fisher Scientific Co. will be used for preparation of calibration solutions. For inductively coupled plasma-atomic emission spectroscopy the calibration and analysis of the samples will be performed according to EPA method 200.7 [Martin and Kopp (ed.), Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio]. Single and multielement standards obtained from SPEX Industries (Metuchen, New Jersey) as well as certified reference samples (e.g., EPA or NBS) will be used to check the instrument calibration.

Instrument standardization will be conducted by subjecting an aliquot of the standard solution to the analytical procedures in the same manner as a sample aliquot and by calibrating the observed instrument response for each standard constituent to the known concentration of that constituent. Matrix effects will be checked by spiking samples and alternate method checks. Any observed matrix effects will be corrected.

Standardization of organic analysis will be conducted using appropriate NBS materials (PAH's, phenols) on a biweekly basis. Periodic quality control samples will be used for a wet chemical operations check.

7. Analytical Procedures

7.1 Extraction and Concentration

All solvent partition/concentration steps are carried out using internal standards. The internal standards (azulene, fluorophenol, and ^{14}C-cresol) are added prior to extraction and are used as a measure of recovery as well as for instrumental calibration. A sample blank (distilled water + internal standards) is run with each set of sample analyses (up to a maximum of eight).

7.2 Analytical Chromatography

A standard mixture (containing the above-mentioned internal standards) is analyzed with each sample set (all samples received on a given date, maximum of eight samples) to verify the response of the instrument, the retention time of the internal standard, and the integration parameters. If any parameter varies more than 10% from the previous standard analysis, corrective action is taken. Such action might include recalibration, detector cleaning, column replacement, etc.

7.3 Gas Chromatography/Mass Spectrometry

Instrumental variables (tuning parameters, etc.) are checked and recorded daily. Calibration curves are checked with each sample set (as above).

7.4 Atomic Absorption (AA) Spectroscopy

All aqueous samples to be analyzed by atomic absorption (AA) spectroscopy will be analyzed by a Perkin-Elmer Model 403 or 603 AA instrument. Flame atomic absorption will be used if the sample contains high enough concentrations of the elements to be determined accurately by this method. If concentrations are lower than this, graphite furnace AA will be used. All samples will be preserved and treated according to standard methods (USEPA 1979) with the following exceptions:

(1) extracts for Hg determination will be preserved by addition to a nitric acid/dichromate solution and worked up for cold vapor flameless AAS (Feldman 1974),

(2) Se will be chelated with 5-nitro-o-phenylene diamine and extracted into toluene before analysis (Talmi and Andren 1974), and

(3) As will be determined by an arsine accumulation-helium glow detector procedure (Feldman 1979).

External reference solutions and EPA multielement standards will be used for instrument calibration. All samples will be analyzed by the standard addition method (USEPA 1979).

7.5 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP)

Multielement analysis will be performed with an Instruments SA, Inc. model JY85 inductively coupled plasma-atomic emission spectrometer (ICP-AES), which contains a 1-m polychromator equipped with exit slits centered at the most sensitive emission line (except for Na, Li, and K) of 35 different elements for simultaneous determinations. A scanning "n + 1" channel is also used either for the determination of an additional element or as an alternate emission line of one of the existing 35 elements. This instrument is controlled by a PDP-11/23 minicomputer, which also handles all data manipulations.

The computer software provided by the manufacturer includes background correction, interelement correction, and blank subtraction algorithms, which are included in the program that automatically changes samples, takes data, etc.

Dilute aqueous solutions containing the analyte are pumped into a cross flow nebulizer, which produces a fine aerosol. The aerosol is carried into the ICP, an extremely hot, flame-like electrical discharge in argon gas, where the analyte species are thermally excited and spontaneously emit radiation characteristic of the elements present. The radiation is measured with the polychromator and monochromator to determine the concentrations of elements in the solution.

Multielement standards from SPEX Industries (Metuchen, New Jersey) are used to calibrate this instrument. At the present time, calibration is performed once each day and periodically checked with an EPA or an NBS standard.

The simultaneous multielement capability of this instrument permits rapid, cost-effective analyses to be performed. Accuracy is generally better than 10% for elements whose concentrations are more than ten times their detection limit, while precision is usually better than 5% relative standard deviation (RSD).

8. Data Analysis, Validation, and Reporting

All data analysis, validation, and reporting conducted for the "Toxicity of Leachates" project will be accomplished through the establishment of a Research Data Management System which incorporates a number of computerized systems (Fig. A-2). Data (inorganic and organic analyses) will be entered into this data management system in accordance with the sample identifier code as described under Section 5. The ICP data will be programmed directly by the analyst; other data will require formatting and entry by the data management group.

A software package entitled Statistical Analysis System (SAS) is leased by ORNL to conduct statistical analyses of the data obtained in the project. This is a well-documented heavily used package produced by SAS Institute, Box 8000, Cary, North Carolina 27511.

The Decision Support System (DSS) is one component of this system and is designed for management-level integration of environmental research data. The DSS includes a plan of study documentation component for determining ongoing research among different sites, a status component for determining the current and proposed research within research sites, and a criteria component for documenting the numeric standards or limits (e.g., EPA/RCRA guidelines) within a research project.

To cope with the problem of accounting for and summarizing the status and results of all samples taken during the project, a Project Results and Tracking System (PRTS) will be included in the validation procedures. The PRTS is designed to ensure that each sample, matched

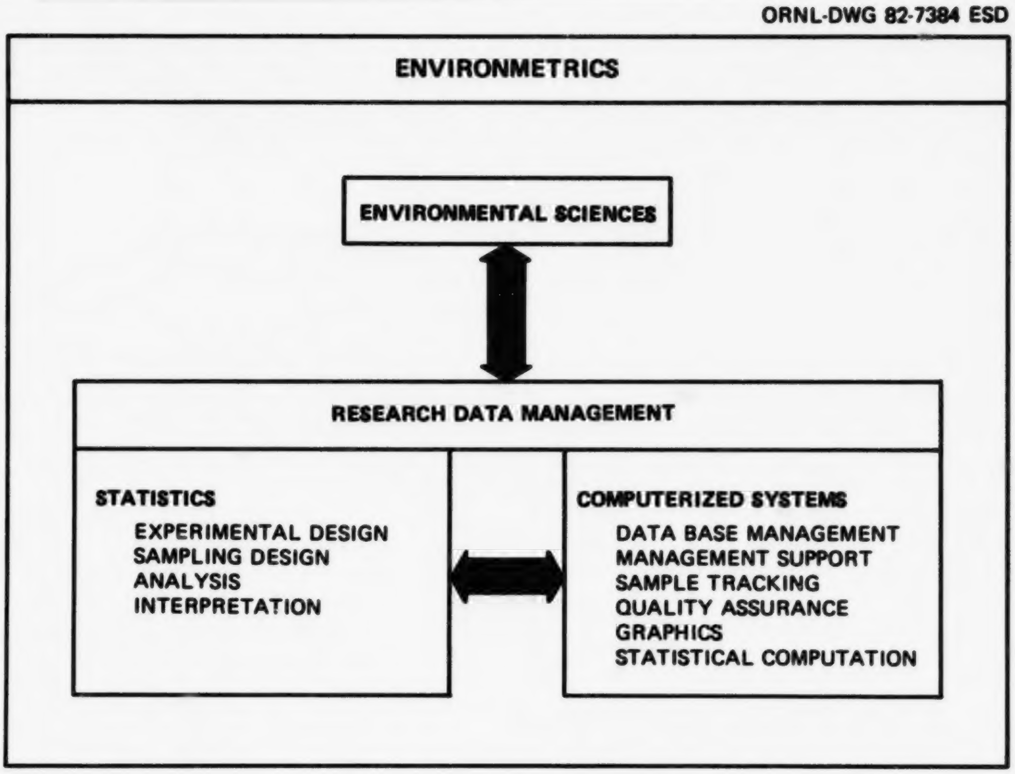

ORNL-DWG 82-7384 ESD
ENVIRONMETRICS
ENVIRONMENTAL SCIENCES
RESEARCH DATA MANAGEMENT
STATISTICS
EXPERIMENTAL DESIGN
SAMPLING DESIGN
ANALYSIS
INTERPRETATION
COMPUTERIZED SYSTEMS
DATA BASE MANAGEMENT
MANAGEMENT SUPPORT
SAMPLE TRACKING
QUALITY ASSURANCE
GRAPHICS
STATISTICAL COMPUTATION

Fig. A-2. Disciplines and activity areas.

with its corresponding characterization and effects data, represents an appropriate estimate of a component of the research design. A PRTS, by automating the bookkeeping procedures, reduces the time and effort often needed to track large numbers of samples across research groups, and it can provide an initial check on validity, completeness, and/or accuracy of the results from each sample. Formal and detailed quality assurance controls are also established in the Quality Assurance System. The Quality Assurance System is a computerized program that checks for the proper syntax, coding, and variable values using criteria developed specifically for the type of data collected by the investigators.

Implementing quality assurance controls on developing and/or extant data bases is necessary to ensure the validity of the results of the research program. The Quality Assurance System for the Toxicity of Leachates project has been developed to assist scientists in detecting potential errors in both qualitative and quantitative data. All major data sheets will have a program written to ensure that the proper syntax and variable values have been recorded and keypunched. The program will document all outlier and syntax errors in the raw data files and will provide an annotated output for resolving other potential errors, such as values outside a variable's existing range, improper lab identification, improper dates, etc. All error definition, recognition, and correction will be accomplished by staff within the program.

A generalized figure representing the data flow for the Toxicity of Leachates project through the Research Data Management System is illustrated in Fig. A-3. As stated earlier, a number of generic computerized systems have been developed to support management inquiries, determine the status of sample analyses and results, detect possible errors in the data, establish computer file structure and manipulation techniques, support graphical displays, and provide statistical computation procedures. A flow diagram showing sample processing and analyses is presented in Fig. A-4. All files are automatically backed up weekly by staff in Computer Sciences, UCCND.

The criterion for flagging possible erroneous data is developed by the investigator and is based on known or possible ranges of values and techniques and methodologies employed. Outliers or extreme data points are identified using an empirical approach rather than any formal statistical decision rules. The investigator first examines outliers for possible measurement or transcription errors. If these are not present, the analyses are conducted with and without the outliers. Data are graphed to investigate residual patterns and are only deleted at the request of the investigator.

ORNL–DWG 82-7382

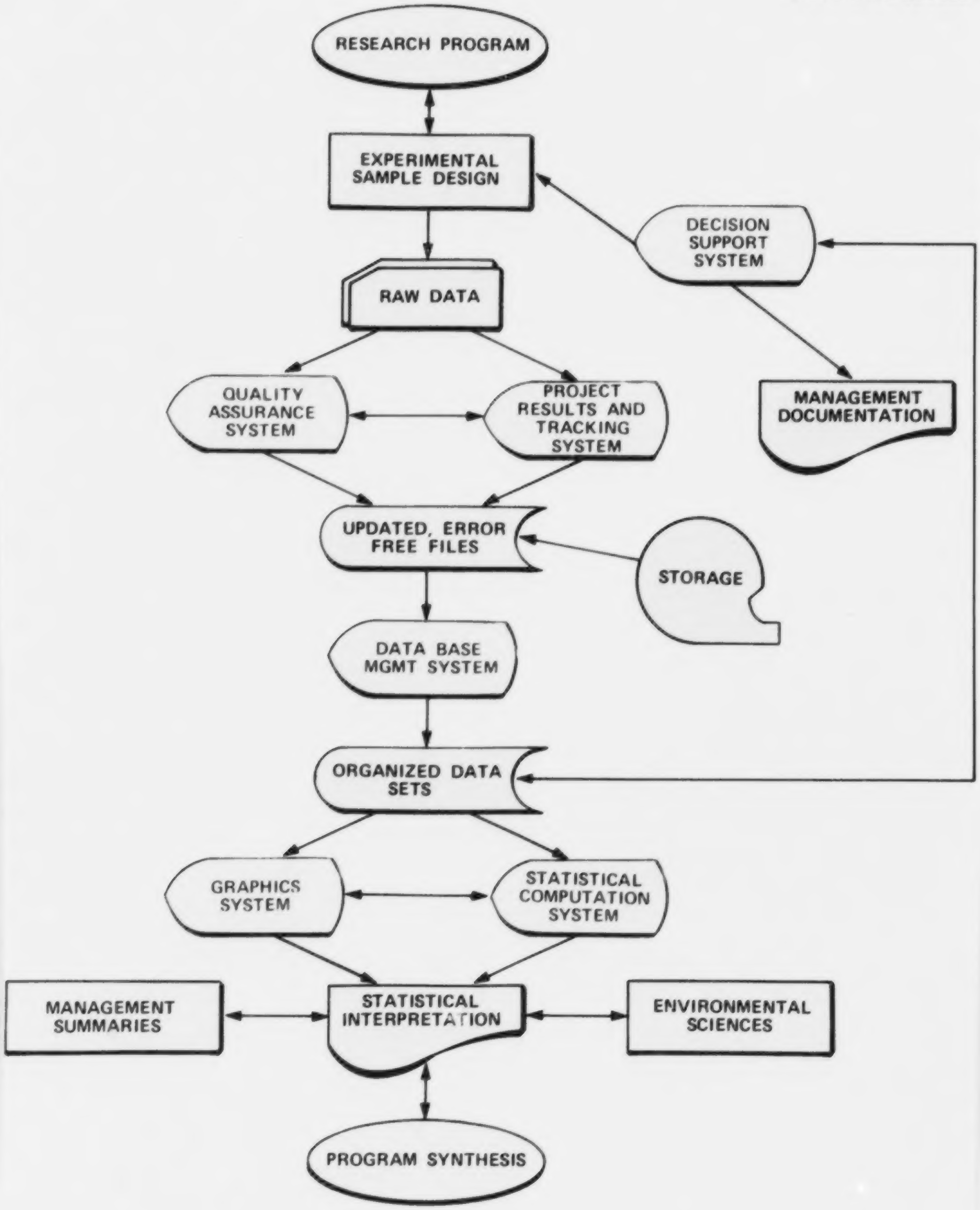

RESEARCH PROGRAM
EXPERIMENTAL SAMPLE DESIGN
DECISION SUPPORT SYSTEM
RAW DATA
QUALITY ASSURANCE SYSTEM
PROJECT RESULTS AND TRACKING SYSTEM
MANAGEMENT DOCUMENTATION
UPDATED, ERROR FREE FILES
STORAGE
DATA BASE MGMT SYSTEM
ORGANIZED DATA SETS
GRAPHICS SYSTEM
STATISTICAL COMPUTATION SYSTEM
MANAGEMENT SUMMARIES
STATISTICAL INTERPRETATION
ENVIRONMENTAL SCIENCES
PROGRAM SYNTHESIS

Fig. A-3. The research data management components.

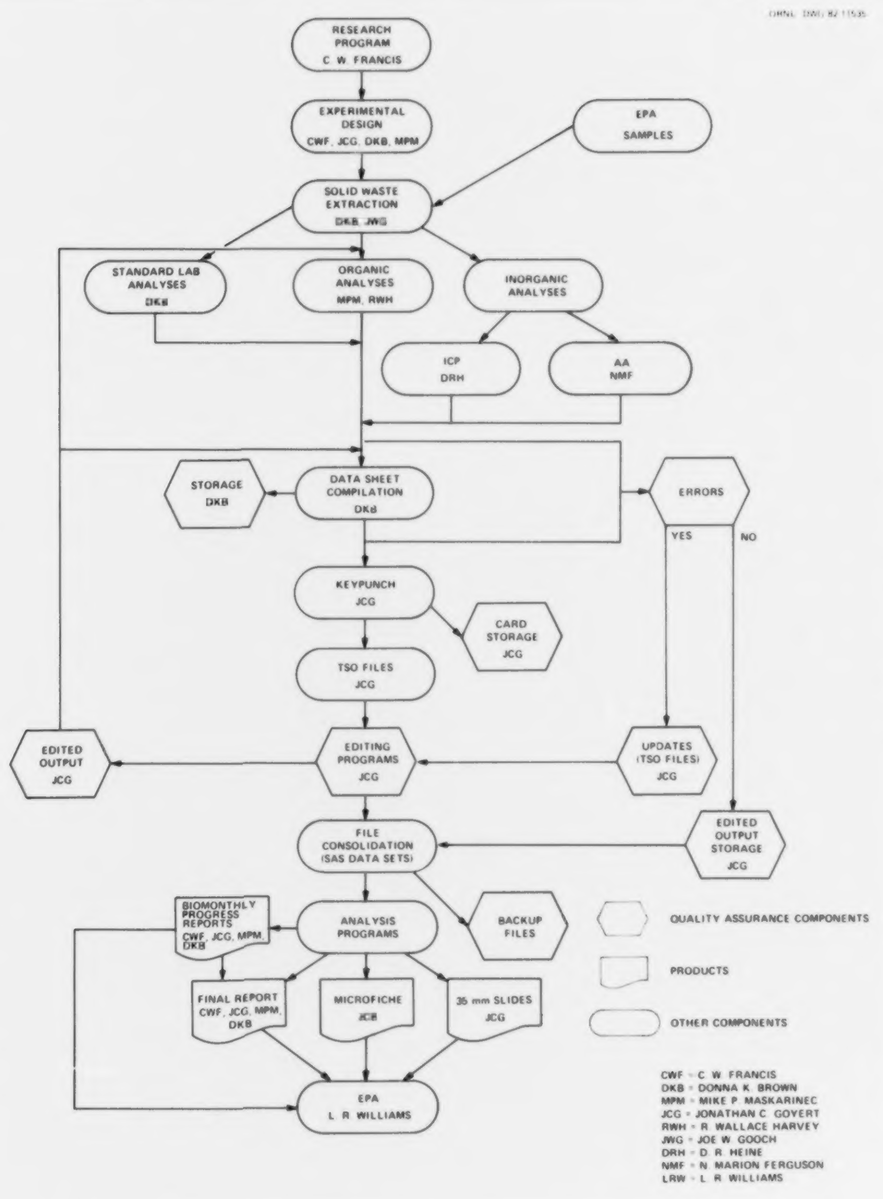

ORNL DWG 82 11535
RESEARCH PROGRAM C. W. FRANCIS
EXPERIMENTAL DESIGN CWF, JCG, DKB, MPM
EPA SAMPLES
SOLID WASTE EXTRACTION DKB, JWG
STANDARD LAB ANALYSES DKB
ORGANIC ANALYSES MPM, RWH
INORGANIC ANALYSES
ICP DRH
AA NMF
STORAGE DKB
DATA SHEET COMPILATION DKB
ERRORS
YES
NO
KEYPUNCH JCG
CARD STORAGE JCG
TSO FILES JCG
EDITED OUTPUT JCG
EDITING PROGRAMS JCG
UPDATES (TSO FILES) JCG
FILE CONSOLIDATION (SAS DATA SETS)
EDITED OUTPUT STORAGE JCG
BIOMONTHLY PROGRESS REPORTS CWF, JCG, MPM, DKB
ANALYSIS PROGRAMS
BACKUP FILES
FINAL REPORT CWF, JCG, MPM, DKB
MICROFICHE JCG
35 mm SLIDES JCG
EPA L. R. WILLIAMS
QUALITY ASSURANCE COMPONENTS
PRODUCTS
OTHER COMPONENTS
CWF = C. W. FRANCIS
DKB = DONNA K. BROWN
MPM = MIKE P. MASKARINEC
JCG = JONATHAN C. GOYERT
RWH = R. WALLACE HARVEY
JWG = JOE W. GOOCH
DRH = D. R. HEINE
NMF = N. MARION FERGUSON
LRW = L. R. WILLIAMS

Fig. A-4. Sample and processing analysis.

9. Internal Quality Control Checks

Internal quality control checks will be conducted in AA and ICP analyses of each set of solid waste extracts to assess precision and accuracy of instrument calibration. The checks consist of: (1) re-analysis of calibration standards to confirm calibration, and (2) analysis of check standards (these are standards of different concentrations from the standards used to calibrate the instrument) with each sample set. Flame AA results should agree within ±5% of the true value. For samples analyzed by graphite furnace containing elements ten times the detection limit, the objective is ±10%, while for samples near the detection limit the objective is 100 to 200%. If the results do not agree within these limits, matrix effects will be checked by spiking samples.

Internal quality control checks for organic analyses will be conducted by inspection of the chromatographic profiles of each standard, solid waste extract, and sample chemical fraction. Any unexpected/unusual chromatographic peaks or features will be noted and interpreted with consideration of instrument malfunction, sample contamination, or true (non-artifactual) occurrence. The use of NBS standard materials will be used to verify instrument performance.

Solid waste extracts and municipal waste leachate analyzed by ICP will be conducted by analyzing two replicate extracts (two aliquots from the same solid waste extraction or leachate samples). Periodic blanks of the relevant extraction medium will be subjected to the same procedures to determine if the samples are receiving external contamination. Additional quality control methods used during analytical analyses are reported in Sections 3, 6, and 7.

10. Performance and System Audits

The system audit will be conducted as a part of the final methods development and validation work, before the routine sample analyses are initiated. The audit will ensure that sample handling, solid waste extraction, fractionation, and analysis and quality control measures are conducted properly and that data calculation, interpretation, storage, and reporting flow correctly.

The performance audit will include the analysis of test materials of concentrations unknown to the chemists performing the analysis. This audit will be performed at least quarterly. To implement this audit, ORNL has requested the EPA project officer to provide a reference solid waste extract containing known concentrations of organics and inorganics for analyses quarterly. Additionally, the ORNL QA office has scheduled a QA audit of this project for May of 1982 in accordance with ORNL Procedure QA-L-8-100.

11. Preventative Maintenance

The chemists assigned to the project are responsible for daily maintenance and upkeep of the analytical instrumentation. Preventive maintenance measures include periodic cleaning of instrument housing ventilation filters, replacement of support gas filters/impurity traps, lubrication of moving parts, etc., as specified by the instrument manufacturers. Instrument repairs are conducted by the manufacturer for those instruments still under warranty, or by the ORNL Instrumentation and Controls Division (I&C) for those no longer under warranty.

Spare parts for many of the instruments are kept in supply by the I&C Division. The I&C Division also provides routine preventative maintenance on electronic equipment in accordance with IPD2, Maintenance Information System Instrumentation Manual. The Plant and Equipment (P&E) Division provides routine preventative maintenance on mechanical equipment in accordance with QA-PE-18/D.1.14.

12. Specific Procedures to be Used Routinely to Assess Data Precision, Accuracy, and Completeness

A. Precision - Precision will be assessed by calculation of the relative standard deviation of repetitive measurements carried out on selected samples, as shown below:

$$RSD_i = 100 \quad \frac{\Sigma\,(X_i-\bar{X}_i)^2}{(n_i-1)}/\bar{X}_i \quad ,$$

where RSD_i = relative standard deviation for measurements of component i,

X_i = individual measurements of component i,

X_i = the average of the measurements of component i, and

n_i = the number of measurements.

The relative standard deviations should not exceed those established in the course of analytical methods of development/validation studies.

B. Accuracy - Analytical measurement accuracy will be assessed in the Performance Audits, the Internal QC Checks, and in the comparison of data on samples shared with other laboratories. In the first two of these measures, the analytical result will be compared with the true result, and the accuracy of measurement of each constituent (A_i) will be calculated as the percentage of difference between the measured value (X_i) and the true value (T_i):

$$A_i = 100\,(X_i-T_i)/T_i \quad .$$

Re-analysis of calibration standards and analyses of check standards should agree to within ±15% of the true value.

C. Completeness - Completeness of data will be evaluated by multiplying the fraction of samples analyzed (number of samples actually analyzed/number of samples planned in expected design which could have been analyzed) by the fraction data generated (number of actual data points generated per sample) and expressing the result as a percentage. A result such as "ND" (component not detected) is considered a data point, while lack of an analysis due to instrument malfunction or sample loss would be classified as a lack of data points. At least 90% of the expected data should be generated. Where possible, reruns of sample material or reanalysis of extracts will be performed to minimize the occurrence of missing data.

13. Corrective Action

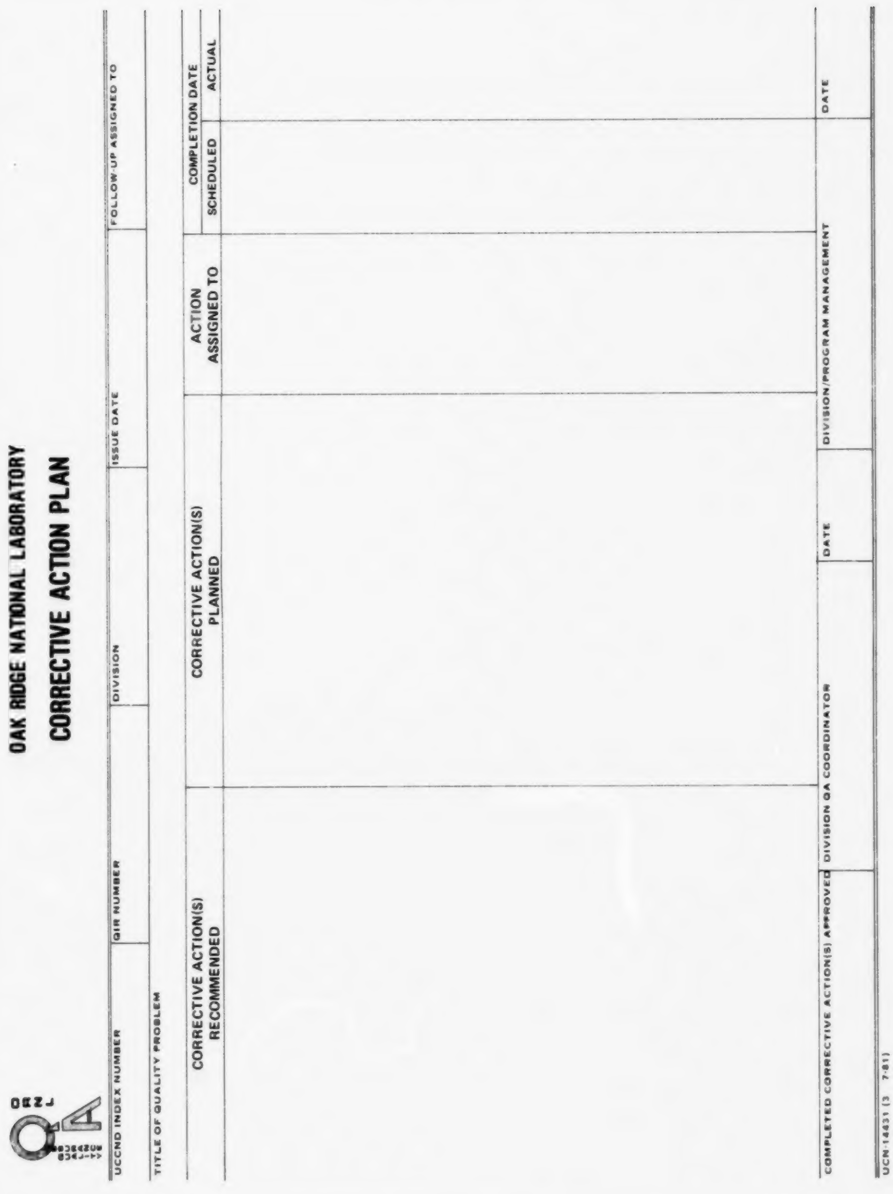
The corrective action to be taken depends on the type of performance deficiency. For deficiencies uncovered in routine internal quality control checks, the actions outlined in Section 9 will be taken. For deficiencies discovered in data evaluation, outlined in Section 8, the following correction actions will be taken:

A. Accuracy - Insufficient accuracy may result from factors such as instrument malfunction, improper instrument calibration, degradation or other changes in the calibrating standards, or improper sample aliquotting. The first three factors may be identified by analysis of a freshly prepared standard. The last cause may be checked only be re-aliquotting the sample. (Aliquots will be held specifically for this purpose.) Improper measurement of sample recovery also can lead to inaccuracy and can be determined only by remeasurement. Samples should be re-analyzed where loss of accuracy is uncovered.

B. Precision - Loss of acceptable precision may be attributed to factors such as instrument malfunction or irreproducible aliquotting. These causes could be checked by repetitive analysis of a standard and distinguished by comparing results obtained in two instruments. Re-analysis of at least selected samples would be required to remedy this deficiency.

C. Completeness - Insufficient data may be caused by sample loss (either sample mishandling or isolation procedure failure), instrument breakdown, or failure to perform the analysis. The potential for sample loss is very low. In the case of instrument breakdown or failure to perform the analysis, the sample analysis should be rescheduled. Corrective action relative to sample loss will be dealt with by making an extraction on original waste.

Significant quality deficiencies are reported to upper ORNL management throughout the ORNL QA program in accordance with procedure QA-L-6-103 (Fig. A-5).



OAK RIDGE NATIONAL LABORATORY

CORRECTIVE ACTION PLAN

UCCND INDEX NUMBER	QIR NUMBER	DIVISION	ISSUE DATE	FOLLOW-UP ASSIGNED TO
TITLE OF QUALITY PROBLEM				

CORRECTIVE ACTION(S) RECOMMENDED	CORRECTIVE ACTION(S) PLANNED	ACTION ASSIGNED TO	COMPLETION DATE	
			SCHEDULED	ACTUAL

COMPLETED CORRECTIVE ACTION(S) APPROVED	DIVISION QA COORDINATOR	DATE	DIVISION/PROGRAM MANAGEMENT	DATE

UCN-14431 (3 7-81)

Fig. A-5. Corrective action plan.

14. Quality Assurance Reports to Management

QA information will be summarized to the EPA Project Officer in each bimonthly data report. Internally in ORNL each division has a quality assurance program (see Fig. A-6). Procedures relative to projects and programs in the respective divisions are outlined in the Divisions' Quality Assurance Program: Environmental Sciences Division's Quality Assurance Program (QA-ES-1-100) and Analytical Chemistry Division's Quality Assurance Program. Each project will be assessed and reviewed periodically. The QA assessment review date schedule is included for the Analytical Chemistry Division (see Fig. A-7).

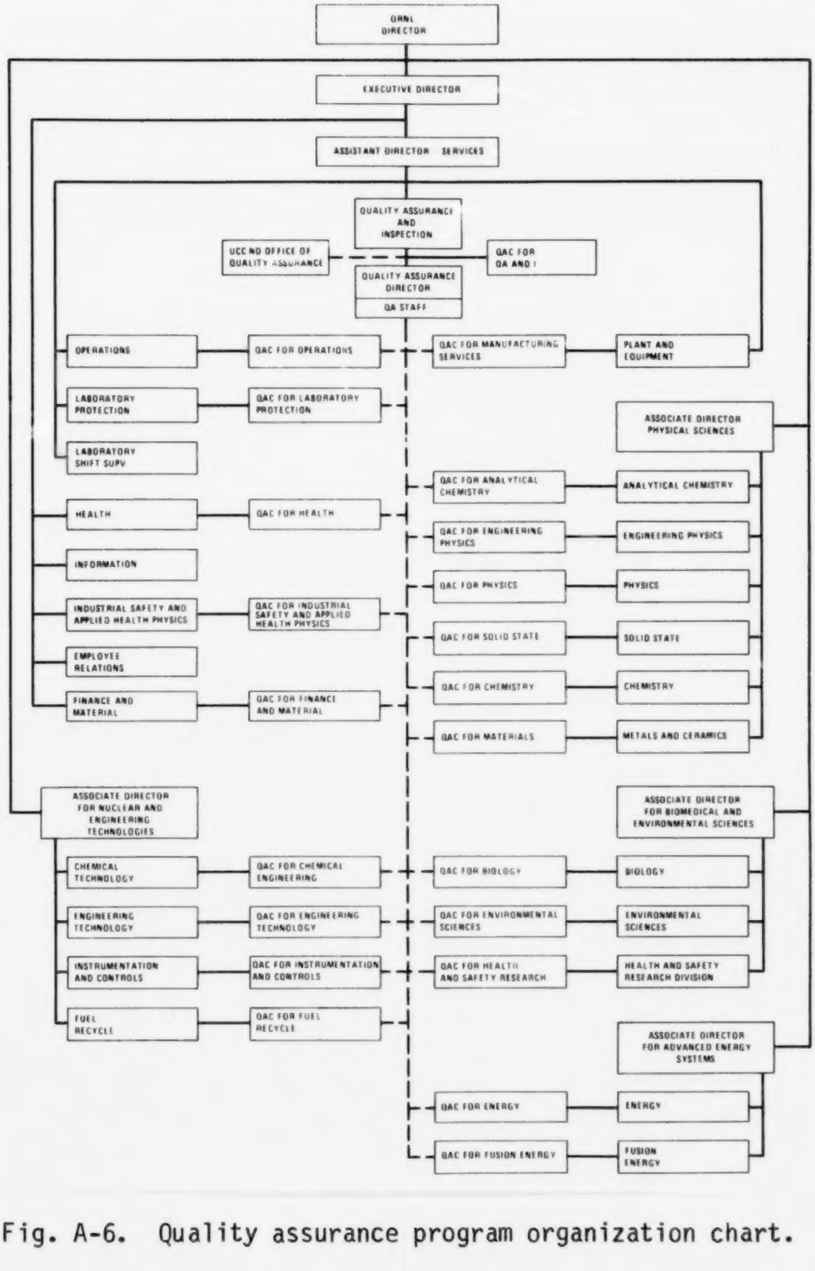

ORNL DIRECTOR
EXECUTIVE DIRECTOR
ASSISTANT DIRECTOR – SERVICES
QUALITY ASSURANCE AND INSPECTION
UCC ND OFFICE OF QUALITY ASSURANCE
QAC FOR QA AND I
QUALITY ASSURANCE DIRECTOR
QA STAFF
OPERATIONS
QAC FOR OPERATIONS
QAC FOR MANUFACTURING SERVICES
PLANT AND EQUIPMENT
LABORATORY PROTECTION
QAC FOR LABORATORY PROTECTION
ASSOCIATE DIRECTOR PHYSICAL SCIENCES
LABORATORY SHIFT SUPV
QAC FOR ANALYTICAL CHEMISTRY
ANALYTICAL CHEMISTRY
HEALTH
QAC FOR HEALTH
QAC FOR ENGINEERING PHYSICS
ENGINEERING PHYSICS
INFORMATION
QAC FOR PHYSICS
PHYSICS
INDUSTRIAL SAFETY AND APPLIED HEALTH PHYSICS
QAC FOR INDUSTRIAL SAFETY AND APPLIED HEALTH PHYSICS
QAC FOR SOLID STATE
SOLID STATE
EMPLOYEE RELATIONS
QAC FOR CHEMISTRY
CHEMISTRY
FINANCE AND MATERIAL
QAC FOR FINANCE AND MATERIAL
QAC FOR MATERIALS
METALS AND CERAMICS
ASSOCIATE DIRECTOR FOR NUCLEAR AND ENGINEERING TECHNOLOGIES
ASSOCIATE DIRECTOR FOR BIOMEDICAL AND ENVIRONMENTAL SCIENCES
CHEMICAL TECHNOLOGY
QAC FOR CHEMICAL ENGINEERING
QAC FOR BIOLOGY
BIOLOGY
ENGINEERING TECHNOLOGY
QAC FOR ENGINEERING TECHNOLOGY
QAC FOR ENVIRONMENTAL SCIENCES
ENVIRONMENTAL SCIENCES
INSTRUMENTATION AND CONTROLS
QAC FOR INSTRUMENTATION AND CONTROLS
QAC FOR HEALTH AND SAFETY RESEARCH
HEALTH AND SAFETY RESEARCH DIVISION
FUEL RECYCLE
QAC FOR FUEL RECYCLE
ASSOCIATE DIRECTOR FOR ADVANCED ENERGY SYSTEMS
QAC FOR ENERGY
ENERGY
QAC FOR FUSION ENERGY
FUSION ENERGY

Fig. A-6. Quality assurance program organization chart.

QA ASSESSMENT REVIEW DATE SCHEDULE
FOR PERIOD ENDING 12/31/1981

DIVISION	DOCUMENT NUMBER	QA ASSESSMENT TITLE	ORIGINATOR	ISSUE DATE	SCHEDULED REVIEW DATE	STATUS
AC	AC-AI-1	IN-LINE ANALYTICAL SENSORS	STRAIN	8/28/1981	9/01/1982	OPEN
AC	AC-BO-1	ANALYSIS OF OCCUPATIONAL/ENVIRONMENTAL SAMPLES	CATON	6/03-1981	6/03/1982	OPEN
AC	AC-BO-2	GASIFIERS FOR INDUSTRY	CATON	6/03/1981	6/03/1982	OPEN
AC	AC-BO-3	GENERATION AND CHEMISTRY OF AEROSOLS	CATON	6/03/1981	6/03/1982	OPEN
AC	AC-BO-4	SMOKING AND HEALTH	CATON	6/03/1981	6/03/1982	OPEN
AC	AC-BO-5	SPECIALIZED ORGANIC ANALYTICAL CHEMISTRY	CATON	6/03/1981	6/03/1982	OPEN
AC	AC-GAL-1	BAUSCH AND LOMB SPECTROPHOTOMETER X 11783	RICKARD	9/07/1979	1/01/1982	OPEN
AC	AC-GAL-12	ATOMIC ABSORPTION SPECTROPHOTOMETER(S) P-E 403, P-E 460	RICKARD	10/23/1979	1/01/1982	OPEN
AC	AC-GAL-13	TRACOR MODEL 222 GAS CHROMATOGRAPH	RICKARD	11/14/1979	1/01/1982	OPEN
AC	AC-GAL-14	ASH FUSION FURNACE	RICKARD	11/12/1979	1/01/1982	OPEN
AC	AC-GAL-15	INDUCTIVELY COUPLED PLASMA SPECTROMETER	STEWART	2/02/1981	2/25/1982	OPEN
AC	AC-GAL-16	LECO OXYGEN DETERMINATOR, RO18	LAYTON	2/05/1981	2/05/1982	OPEN
AC	AC-GAL-17	ION CHROMATOGRAPH, DIONEX MODEL 16	KELLER	2/18/1981	2/20/1982	OPEN
AC	AC-GAL-2	FISHER TITATOR	RICKARD	9/07/1979	1/01/1982	OPEN
AC	AC-GAL-3	TECHNICON AUTOANALYZERS	RICHARD	10/22/1979	1/01/1982	OPEN
AC	AC-GAL-4	FLUOROPHOTOMETER - SINTERING FURNACE (FLUOROMETRIC URANIUM EQUIP)	RICKARD	10/22/1979	1/01/1982	OPEN
AC	AC-GAL-5	TEKTRONICS 4025 COMPUTER TERMINAL	RICHARD	10/23/1979	1/01/1982	OPEN
AC	AC-MES-1	OPTICAL EMISSION SPECTROMETER I - PASCHEN	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-10	DUPONT 21-490B/21-094B GAS CHROMATOGRAPH-MASS SPECTROMETER	RAINEY		1/01/1982	OPEN

Fig. A-7. Analytical Chemistry Divison QA assessment schedule.

QA ASSESSMENT REVIEW DATE SCHEDULE
FOR PERIOD ENDING 12/31/1981

DIVISION	DOCUMENT NUMBER	QA ASSESSMENT TITLE	ORIGINATOR	ISSUE DATE	SCHEDULED REVIEW DATE	STATUS
AC	AC-MES-11	ORNL SINGLE-STATE GAS CHROMATOGRAPH-MASS SPECTROMETER	RAINEY	11/08/1979	1/01/1982	OPEN
AC	AC-MES-12	SPARK SOURCE MASS SPECTROMETER - 2026	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-13	AEI MS-50/DS-50 MASS SPECTROMETER-DATA SYSTEM	RAINEY	11/08/1979	1/01/1982	OPEN
AC	AC-MES-14	ORNL THREE STAGE MASS SPECTROMETER - ORG.	RAINEY	11/08/1979	1/01/1982	OPEN
AC	AC-MES-15	MICROMASS 1201 GAS MASS SPECTROMETER	SITES	11/08/1979	1/01/1982	OPEN
AC	AC-MES-2	OPTICAL EMISSION SPECTROMETER II - WADSWORTH	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-3	ION MICROPROBE MASS SPECTROMETER	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-4	SPARK SOURCE MASS SPECTROMETER - MS-7	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-5	SPARK SOURCE MASS SPECTROMETER - MS-702R	CHRISTIE	11/08/1979	1/01/1982	OPEN
AC	AC-MES-6	2-STAGE MASS SPECTROMETER - RAL	SMITH	11/09/1979	1/01/1982	OPEN
AC	AC-MES-7	SINGLE-STAGE MASS SPECTROMETER - RAL	SMITH	11/09/1979	1/01/1982	OPEN
AC	AC-MES-8	2-STAGE MASS SPECTROMETER - TRU	SMITH	11/09/1979	1/01/1982	OPEN
AC	AC-MES-9	3-STAGE MASS SPECTROMETER - RAL	SMITH	11/09/1979	1/01/1982	OPEN
AC	AC-NRAS-1	COMPUTER BASED PULSE HEIGHT ANALYSIS SYSTEM ND6620	EMERY	2/20/1980	1/01/1982	OPEN
AC	AC-NRAS-2	OAK RIDGE RESEARCH REACTOR PNEUMATIC TUBE	EMERY	5/01/1980	1/01/1982	OPEN
AC	AC-NRAS-3	COMPUTER BASED PULSE HEIGHT ANALYSIS SYSTEM, BLDG 3042	EMERY	5/01/1980	1/01/1982	OPEN
AC	AC-NRAS-4	DATA ACQUISITION SYSTEM, ND 6603, 6-49, 4500S	SCOTT	5/01/1980	1/01/1982	OPEN

Fig. A-7. Continued.

QA ASSESSMENT REVIEW DATE SCHEDULE
FOR PERIOD ENDING 12/31/1981

DIVISION	DOCUMENT NUMBER	QA ASSESSMENT TITLE	ORIGINATOR	ISSUE DATE	SCHEDULED REVIEW DATE	STATUS
AC	AC-NRAS-5	HIGH FLUX ISOTOPE REACTOR PNEUMATIC TUBE	BATE	7/02/1980	7/31/1982	OPEN
AC	AC-NRAS-6	COMPUTER BASED PULSE HEIGHT ANALYSIS SYSTEM AT BLDG 7900	BATE	7/02/1980	7/31/1982	OPEN
AC	AC-PM-1	PHYSICO-CHEMICAL ANALYSES GROUP	RICCI	11/05/1979	1/01/1982	OPEN
AC	AC-RMAL-1	IN-CELL PIPET	LAING	11/08/1979	1/01/1982	OPEN
AC	AC-RMAL-2	IN-CELL ANALYTICAL BALANCE	LAING	11/08/1979	1/01/1982	OPEN
AC	AC-RMAL-3	IN-CELL FURNACE	LAING	11/08/1979	1/01/1982	OPEN
AC	AC-RMAL-4	IN-CELL SPECTROPHOTOMETER	LAING	11/08/1979	1/01/1982	OPEN
AC	AC-RMAL-5	HOT-CELL MANIPULATORS	LAING	11/08/1979	1/01/1982	OPEN
AC	AC-RMAL-6	X-RAY FLUORESCENCE ANALYZER	STEWART	2/02/1981	2/02/1982	OPEN
AC	AC-TRU-1	PULSE-HEIGHT ANALYZER	COOPER	11/13/1979	1/01/1982	OPEN
AC	AC-TRU-2	PROPORTIONAL COUNTERS	COOPER	11/13/1979	1/01/1982	OPEN
AC	AC-TRU-3	TITRATOR	COOPER	11/12/1979	1/01/1982	OPEN
AC	AC-TRU-4	BAUSCH AND LOMB SPECTROPHOTOMETER	COOPER	11/12/1979	1/01/1982	OPEN
AC	AC-TRU-5	REMOTE PIPETTOR	COOPER	11/12/1979	1/01/1982	OPEN
AC	AC-TRU-6	GEIGER-MUELLER COUNTER	COOPER	11/13/1979	1/01/1982	OPEN
AC	AC-TRU-7	GAMMA SCINTILLATION COUNTER	COOPER	11/13/1979	1/01/1982	OPEN
AC	AC-TRU-8	NEUTRON COUNTER	COOPER	11/13/1979	1/01/1982	OPEN
AC	AI-2	LASER APPLICATIONS	WHITTEN	9/02/1981	9/01/1983	OPEN
AC	AI-3	REMOTE PIPETTOR AND TITRATOR	KLATT	9/10/1981	10/01/1982	OPEN

Fig. A-7. Continued.

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16. Distribution List

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APPENDIX B

FY-1982 Work Plan

Toxicity of Leachates
Revised 3/25/82

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Interagency Agreements
Between

U.S. Department of Energy
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OAK RIDGE NATIONAL LABORATORY

"TOXICITY OF LEACHATES"

Summary of FY-1982 Workplan
(Revised 3/25/82)

INTRODUCTION

The objective of this research is to develop a second generation laboratory extraction procedure, henceforth known as EP-III, to test mobility of inorganic as well as organic constituents of industrial wastes co-disposed with municipal wastes in a landfill environment. The desirable characteristics of EP-III include:

1. Ability to simulate leaching in a landfill containing municipal (95%) and industrial (5%) wastes.
2. Compatibility with biological toxicity tests (mutagenic, aquatic, and terrestrial).
3. Relatively inexpensive to conduct in terms of time, equipment, and personnel.

STRATEGY

The strategy proposed by Oak Ridge National Laboratory (ORNL) for the development of EP-III will focus on:

1. Determining in the laboratory the quantities of inorganic and organic constituents leached from a variety of industrial wastes by a particular municipal waste leachate.
2. Comparing the extraction characteristics of the above municipal waste leachate to those of laboratory methods (combinations of extraction procedures with artificial extraction media), and

3. Testing the ability of the laboratory extraction methods to simulate the leaching of industrial wastes under field conditions using large-scale lysimeters containing municipal (95%) and industrial (5%) wastes.

The proposed research will involve both laboratory and field work. The initial laboratory effort will be directed toward evaluating the extraction conditions that are most aggressive in removing inorganic and organic constituents from selected industrial wastes by a particular municipal waste leachate. The municipal waste leachate selected for this study will be obtained from a lysimeter located at the U.S. Army Corps of Engineers Waterways Experiment Station (WES), Vicksburg, Mississippi. The extraction procedure (column aerobic, column anaerobic, or rotary batch) found to be most aggressive will serve as baseline data to be simulated by the laboratory procedure developed for EP-III. The laboratory variables to be investigated in this phase of the work will consist of the type of extraction procedure (up-flow column or batch rotary) and type of artificial extraction media (acetate buffer, CO_2-saturated water, distilled water, or synthetic leachate).

Concentrations of inorganic and organic constituents found in waste leachate from field demonstration large-scale lysimeter experiments containing waste in a 95% municipal to 5% industrial scenario will be compared to those observed in the laboratory extractions. Results from both the laboratory and field studies will be combined and compared so that the relationship between laboratory extraction methods and actual field validations can be determined. By comparing laboratory extraction tests with field validations, the potential toxicity of industrial wastes co-disposed with municipal wastes can be examined and evaluated.

LABORATORY STUDIES

A. Objective:

Establish the laboratory extraction method (procedure and medium) that most closely simulates the leaching characteristics of a municipal waste leachate (MWL) in terms of organics and inorganics extracted.

B. Approach:

1. Determine the amount of organic and inorganic chemical constituents removed from four different industrial wastes using three extraction procedures. MWL from WES will be used as the extraction media and will serve as a baseline control to compare against all artificial extraction media in part 2.

   The four industrial wastes will consist of two organic wastes, a waste containing both organic and inorganic contaminants, and a waste predominantly inorganic in character.

   The three extraction procedures will consist of:

   (a) up-flow column - aerobic
   (b) up-flow column - anaerobic
   (c) rotary extractor - aerobic

2. Compare the results from part 1 with the amount of organic and inorganic chemical constituents removed from the same four industrial wastes using two extraction procedures with each of four artificial extraction media.

The two extraction procedures will consist of:

(a) an up-flow column and

(b) a batch rotary extractor.

The four extraction media will consist of:

(a) 0.1 N sodium acetate buffer pH 5,

(b) CO_2-saturated deionized distilled water,

(c) deionized distilled water, and

(d) synthetic MWL that simulates WES/MWL.

C. Experimental Design:

The experiment will consist of a factorial arrangement of 11 treatments and four industrial wastes in a randomized block design with two blocks (time) per treatment-waste combination. The 11 treatments will consist of the eight (procedure x media) laboratory methods plus the three WES/MWL extractions.

D. Analysis:

An analysis of variance will be conducted on the ranked sums (Attachment A) to determine if there are any differences in the amount of organic and inorganic chemical constituents removed by the various extraction procedures and media. Additional analyses will be conducted to determine if there are any overall differences in: (1) the batch versus column extraction procedure, (2) the distilled water, synthetic leachate, and WES/MWL media, and (3) the interaction among the two procedures and the three extraction media. The eight laboratory methods (2 procedures x 4 media) will be compared to the three WES/MWL extractions using a multivariate pattern analysis to determine which of the eight laboratory extraction methods is most similar in chemical composition to the three WES/MWL extractions. An analysis will also be conducted to determine if there are any differences in the amount of organics and inorganics removed by the WES/MWL using the three extraction procedures.

FIELD STUDIES

A. Objectives:

1. Test the ability of various laboratory extraction methods to simulate the leaching characteristics of industrial wastes in large-scale field lysimeter experiments containing wastes in a 95% municipal to 5% industrial scenario.
2. Evaluate the aggressiveness relative to age of a municipal waste leachate to extract contaminants from industrial wastes.

B. Approach:

Municipal waste leachate from two large-scale lysimeters (1.8 m in diameter and 3.6 m in height) will be diverted to 16 columns/lysimeter containing four industrial wastes (the same wastes used in the laboratory studies). For each lysimeter, one-half of the columns (4 wastes x 2 replicates) will be used to compare the 95% municipal and 5% industrial waste scenario to the laboratory extraction studies. The remaining columns will be used to evaluate the relative aggressiveness of the municipal waste leachate as a function of age of the leachate.

C. Experimental Design:

The experiment will consist of a randomized block design with four treatments and two blocks (lysimeters). The experiment will be replicated twice to test the block by treatment interaction.

D. Analysis:

An analysis of variance will be conducted to determine if there are any differences in the amount of organic and inorganic chemical constituents removed from the four industrial wastes by the municipal waste leachate. An analysis will also be conducted to see if there are any differences in leachate quality between the two lysimeters. A multivariate pattern analysis will be used to determine which of the laboratory extraction methods most closely simulates the chemical constituents derived from the field lysimeters. The results from the laboratory studies and the field studies will be combined and statistically analyzed to determine the laboratory method (EP-III) that most closely simulates the mobility of inorganic as well as organic constituents of industrial wastes co-disposed with municipal wastes in a landfill environment.

1. INTRODUCTION

To evaluate the potential toxicity of a leachate from an industrial waste that has been co-disposed with a municipal waste, a laboratory extraction procedure is needed that models the leaching action the waste would undergo when disposed of with a municipal waste. Currently, under RCRA, toxicity is determined by the EP toxicity test procedure (40 CFR 261.24). Toxicity criteria are based on the concentrations of eight elements in the Primary Drinking Water Regulations (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag), four pesticides (Endrin, Lindane, Methoxychlor, Toxaphene), and two herbicides (2,4-D, and 2,4,5-TP Silvex) observed in the extract. The EP is used as a regulatory test to classify a waste relative to a landfill management scenario. The EP has a number of limitations, the most important being that a waste containing other toxicant materials is not included in the present criteria. For example, the EP does not model the effects that the higher molecular weight organics present in a municipal leachate can have on the leaching of a solid waste. Other experimental factors include the effectiveness of extraction, the deficiency of expressing kinetic relationships of components extracted, relevance to real-world leachates, etc. In terms of applying biological testing to EP extracts, the EP is severely limited in that the acetic acid used in the procedure interferes with aquatic toxicity and phytotoxicity testing protocols (Epler et al. 1980).

The objective of the FY-1982 research at ORNL is to develop an extraction test for solid wastes that: (1) models the leaching action a waste would undergo when disposed of, along with a municipal waste, in a municipal waste landfill following a 95/5 (weight fraction of municipal and industrial waste) co-disposal scenario; and (2) is compatible in aquatic toxicity and phytotoxicity testing protocol. This proposed extraction procedure will be henceforth referred to as EP-III.

2. DEVELOPMENT OF EP-III

The major characteristics of EP-III are:

1. It should simulate leaching in a landfill containing municipal (95%) and industrial (5%) wastes (by weight).
2. It has to be compatible with biological testing protocol (mutagenic, aquatic, and phytotoxic).
3. It should be relatively inexpensive to conduct in terms of time, equipment, and personnel.

2.1 Leaching Media Requirements

A synthetic municipal landfill leaching medium is needed to model leaching that occurs in a landfill where an industrial waste is co-disposed with municipal refuse. The characteristics of a municipal landfill leachate will vary widely depending on the municipal refuse composition and state of decomposition. Even for individual samples of municipal refuse it would be impossible to duplicate the leachate composition over time because of its complexity and varying stability to biological degradation. Laboratory leachates using municipal refuse and water are possible to produce; however, reproducing such leachates and maintaining stability are impractical for a test protocol. Rather than attempting to define the leachate characteristics emanating from a defined standard landfill, it is more realistic to develop a synthetic leachate that models leachate of maximum aggressiveness. Such a model leachate will also represent likely mismanagement scenarios, thus adding a degree of conservatism in screening wastes for toxicity.

No one synthetic leachate will model all municipal solid waste leachates; however, some of the characteristics of the more aggressive leachates can be used as a model leachate. Typical characteristics simulating that of a municipal landfill are: (1) low pH (4-6), (2) low redox potential (anoxic environment), (3) mild to high ionic strength (0.05-0.1 M), and (4) high complexation ability.

A low molecular weight carboxylic acid, acetic acid, was used in EP-I to acidify the solid waste suspension to pH 5. The EP-I satisfied items 1 and 3 of the above listed requirements, and for most wastes it has been shown to be more effective than water for removing toxic metals from waste. However, for most wastes, acetic acid is not as effective as water in removing nonpolar organics, and the acetic acid interferes in the phytotoxicity and aquatic toxicity tests. Thus, there is a need to develop a model synthetic extractant that aggressively removes inorganic and organic contaminants from wastes and one that can also be used in biotesting of the resulting leachate. Use of a biodegradable organic acid in the EP-III has to be eliminated from consideration in that such an acid will inherently interfere in the biotesting protocol. Use of inorganic acids such as H_2SO_4 and HCl to acidify solid waste suspensions to pH 5 have also interfered in the phytotoxicity and aquatic toxicity tests. One extracting medium that appears to be a viable alternative is carbonic acid. It is an aggressive leachate from the standpoint of acidity, it is more representative of the acidity source in landfills than mineral acids such as HCl, HNO_3, or H_2SO_4, and under standard conditions of temperature and pressure it should not be inhibitory in any of the biological testing protocols. Bause and McGregor (1980) proposed and evaluated this extractant using the same liquid-to-solid ratio in a batch-type extraction as the EP (20:1) and found that the carbonic acid medium and EP extracted similar quantities of toxic trace metals from four fossil energy solid wastes. Its effectiveness in removing organic compounds from solid wastes has been untested.

2.2 Extraction Procedures

The agitation procedures for conducting the EP have varied from using stirring paddles in stainless steel vessels (glass vessels on rotary agitators) to stirring in glass vessels using commercially available magnetic stirring devices. However, the basic premise has remained the same; that is, the procedure is a batch-type extraction using a final liquid-to-solid ratio of 20:1 during the agitation period of 24 h. The basic principle is to ensure adequate mixing between the solid and aqueous phase. The high liquid-to-solid ratio (20:1) promotes dispersion of many finely textured wastes (organic-laden sludges, etc.) which make filtering a slow and time-consuming effort. To conduct a variety of toxicity tests and the required inorganic and organic analysis, it is necessary to collect as much as 6 L of effluent (Table B-1). This may take as long as 1 to 2 d to filter some of the

TYPIST PROOFER CORRECTOR

TABLE B-1. AMOUNT OF EXTRACT NEEDED FOR VARIOUS ANALYSES[a] AND BIOTESTS

Analyses:	Extract needed (mL)
Inorganics (NIPDWS)	750
Organics	1,000
Bioaccumulation	500
Biotests[b]	
Mutagenicity	1,000
Aquatic (*D. magna* acute)	1,000
Phytotoxicity (root elongation, 2 species)	1,000
Total	5,250

[a] Assumes single determination.

[b] Assumes no dilution.

TYPIST PROOFER CORRECTOR

samples through the 0.45-μm membrane filter (even using a pressure filter apparatus at 75 psi). Recent work at ORNL has shown that the up-flow column extraction procedure removed more nonpolar organic compounds (extracts were collected directly on XAD-2 resins) than the 20:1 batch-type extraction (the common extraction medium being double distilled water). Other work has indicated that volatile constituents are not as easily lost in a closed extraction system (such as the rotary extractor) versus an open system. The column extraction procedure merits more research, and, contrary to previous beliefs, it is not as time-consuming nor is it as nonreproducible relative to the batch extractions as implied in previous investigations. Major equipment costs for column extractions appear to be comparable to batch extractions with a rotary extractor (Table B-2). The important fact is that not many investigators have experimented with an up-flow column as an alternative.

3. PERFORMANCE CRITERIA FOR EP-III

The principal performance criteria for EP-III will be (1) how well it simulates the leaching characteristics of a municipal waste leachate, and (2) its compatibility with biological toxicity testing protocols (mutagenic, aquatic, and phytotoxic).

3.1 Laboratory Studies

The objectives of the laboratory studies are twofold:

1. Establish a data base that represents the leaching characteristics of a municipal waste leachate (MWL) on industrial wastes, and

TABLE B-2. MAJOR EQUIPMENT NEEDS AND ESTIMATED COSTS FOR PERFORMING A BATCH VS COLUMN EXTRACTION[a]

Batch extraction		Column extraction	
Item	Estimated cost	Item	Estimated cost
Rotary extractor	$2,000	Pressure pump[b]	$ 500
Glass vessels (32-L capacity)	45	Glass column with adjustable plungers	130
Filtration apparatus (pressure)	1,400		
Filters (per sample)[c]	15-150		

[a] Assume both are closed extractions, with no pH adjustments, using organic-laden wastes, to produce 6 L of extract.

[b] Average cost for pump, prices vary from $200-2,000.

[c] Disposal item, number needed will vary with sample.

TYPING PHOTOMASTER - STANDARD 6" SINGLE COLUMN FORMAT

2. Develop a laboratory extraction method using a selected procedure and a synthetic medium that best simulates the leaching of industrial wastes by MWL's.

3.1.1 Waste Selection: Four industrial wastes will be utilized for all research. The four wastes will be selected from those listed in Table B-3 and will consist of two organic wastes (tentatively Nos. 1 and 5): a waste containing both organic and inorganic contaminants (either No. 3, 6, or 7 depending on bulk analyses, physical properties, and availability), and a waste predominantly inorganic in character (either No. 2, 4, or 8). Initially major organic and inorganic constituents will be identified in each waste to target the important potential contaminants. This information will be used to select the four most appropriate wastes based on (1) classes of hazardous organic compounds, (2) concentrations of toxic inorganic constituents (predominantly those elements listed in the interim primary drinking water standards), (3) combinations of toxic inorganic and organic compounds, and (4) potential contaminants amenable to target analyses (i.e., those contaminants found in the industrial waste that are different or contained at concentrations sufficiently higher than that observed in the municipal waste leachate). Wastes will not be selected relative to their compatibility with any type of extractor.

3.1.2 Approach: Baseline experiments relative to the extraction capacity of municipal waste leachate (MWL) will be conducted using the leachate obtained January 27, 1982, from the Waterways Experimental Station (WES), Corps of Engineers, Vicksburg, Mississippi.

TABLE B-3. DESCRIPTION AND PRELIMINARY INFORMATION RELATIVE TO THE INDUSTRIAL WASTES TO BE USED IN THE STUDY[a]

ORNL-DWG 82 11534

WASTE NO.	WASTE DESCRIPTION	RCRA CLASSIFICATION[b]	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Ni	Cn	VOLATILE	PAH	CHLORINATED HYDROCARBONS	POLAR ORGANICS	NON-POLAR ORGANICS	HIGH SOLIDS CONTENT	LOW SOLIDS CONTENT	ORGANIC	INORGANIC	PHENOLS	REMARKS
1	WASTE OIL RECLAIMING CLAY	NH											X	X		X	X			X		X	
2	PETROLEUM REFINING INCINERATOR ASH (D007)	H	X			X	X											X			X		
3	PAINT PRODUCTION SLUDGE (D001, F003, F005)	H	(MAY ALSO CONTAIN HIGH Pb AND Cr)										X	X		X	X			X			
4	ELECTROPLATING WASTEWATER SLUDGE (F006)	H			X	X					X	X									X		
5	HEAVY ENDS AND COLUMN BOTTOMS FROM PRODUCTION OF TRI AND PERCHLOROETHYLENE (KO30)	H											X	X	X	X	X			X			
6	APISEPARATOR SLUDGE AND DAF FLOAT (KO48 AND KO51)	H				X	X							X		X	X		X	X			
7	AMMONIA STILL LIME SLUDGE FROM COKING OPERATIONS (KO60)	H	X									X		X		X	X			X	X	X	
8	CAUSTIC FILTER SLUDGE (D009)	H						H												X			1.0–5.0% Hg BY WEIGHT

[a] COLLATED FROM INFORMATION PROVIDED BY TODD KIMMELL, OSW/EPA HQT.

[b] NH = NONHAZARDOUS UNDER RCRA, H = HAZARDOUS.

Approximately 150 L of MWL in 37 3.8-L (1 gal) containers were collected under anaerobic conditions. This leachate is currently being stored under refrigerated conditions. It will be used to extract the four industrial wastes. Extractions will be conducted under aerobic conditions in a rotary extractor at a liquid to solid ratio of 20:1 and under both anaerobic and aerobic conditions in an up-flow column using the same quantity of waste and the effluent collected when the liquid to solid ratio of 20:1 is reached. The extracts will be filtered through glass fiber filters for organic analyses (effective pore diameter approximately 0.7 μm) and 0.45-μm membrane filters for inorganic analyses.

The quantities of inorganic and organic constituents removed from the four industrial wastes with the WES/MWL by the most aggressive of the three extraction procedures will be considered most representative of leaching in a co-disposal environment. We have established, a priori, a four-step protocol for choosing the extraction procedure that is most aggressive across all constituents tested. The first step of the protocol ranks the concentrations of each constituent from least aggressive to most aggressive. The second step groups all the constituents into target categories; NIPDWS inorganics and/or toxic organics (hazardous constituents listed in Appendix VIII, 40 CFR 261.24) and then sums the ranks within a category. The third step ranks the sums within each category. The fourth step sums the ranks across categories, resulting in an overall rank sum that is then statistically analyzed. A short example of such ranking is provided in Attachment A. These data will provide the following information:

1. Establish if significant occur between aerobic and anaerobic column extractions with municipal waste leachate.
2. Determine if differences occur between batch and column extractions with a number of artificial extraction media.
3. Establish baseline data relative to the extraction capabilities of a municipal waste leachate.

The pattern (relative to concentration and distribution) of inorganic and organic constituents extracted by the most aggressive extraction procedure (either anaerobic or aerobic up-flow column or aerobic rotary) using the WES/MWL will be compared to those patterns obtained from the eight laboratory extraction methods (two extraction procedures and four artificial extraction media). The same four industrial wastes will be used.

The two extraction procedures will consist of:

(a) an up-flow column and

(b) a batch rotary extractor.

The four extraction media will consist of:

(a) 0.1 N sodium acetate buffer pH 5,

(b) CO_2-saturated deionized distilled water,

(c) deionized distilled water, and

(d) synthetic MWL that simulates WES/MWL.

The rationale for selecting the extracting media is as follows:

EP-I: The acetic acid pH 5 extraction is a regulatory protocol that has never been compared to the leaching capabilities of a municipal waste leachate. It is possible that the EP-I does simulate the extraction of municipal waste leachates and thus will be included for comparative purposes in the experimental design.

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CO_2-Saturated Deionized Distilled Water: This medium best simulates the pH and anoxic conditions of landfill leachates without incorporating biodegradable organics into the medium. It should also be compatible with biotesting protocols.

Deionized Distilled Water: This medium is included for comparative purposes.

Synthetic Municipal Waste Leachate: This medium which will contain the major organic and inorganic components of the WES municipal waste leachate is intended to simulate the extracting capabilities of the collected leachate. Incorporation of this medium will provide information relative to the importance of organic and inorganic components of the WES leachate to remove various contaminants from the five industrial wastes. Tentatively, the organic components suggested are 500 ppm each of C_2, C_4, and C_6 carboxylic acids.

3.1.3 Quality Control: A description of the quality control for the project is available in the April 15, 1982, "Quality Assurance Project Plan - Toxicity of Leachates Project" (Appendix A of this report). Specifically, each 3.8-L (1 gal) aliquot MWL collected at WES will be analyzed for organic (principally carboxylic acids by high pressure liquid chromatography) and inorganic constituents (inductive coupled plasma-atomic emission spectrometry, atomic absorption spectroscopy, and anionic chromatography). Preliminary analysis of the WES/MWL indicates that target organic compounds can be used to assess leachability. In cases where concentrations of the target constituents are observed in the MWL (both organic and inorganic), these concentrations will be subtracted from the concentrations found in the leachate produced on interacting the MWL and industrial waste. Duplicate analyses for organic and inorganic constituents will be conducted on the leachates (such analysis may not be conducted if analytical accuracy and precision for that analysis is considered to be less than 10%).

3.1.4 Supplementary Study: Compatibility of Extraction Media to Toxicity Tests: A supplementary study will be carried out to determine which of the extraction media can be used with toxicity tests. The toxicity tests to be considered include: (1) an alga growth inhibition test, (2) Daphnia magna acute immobilization test and reproduction test, and (3) a fish acute toxicity test; these tests are found in the document "OECD Guidelines for Testing of Chemicals." Extraction media posing potential inherent toxicity characteristics will be tested in a series of dilutions (including 1:100 and 1:000), with at least one of the toxicity tests mentioned above. This information will aid in determining which of the proposed extractants satisfy the characteristic of being compatible with bioassays.

3.2 Field Studies - (95/5) Scenario

3.2.1 Objectives and Approach: The major objectives are to (1) determine at what point in time and at what volume of leachate the concentration of the inorganic and organic contaminants the highest in the leachate from the industrial wastes, (2) compare these concentrations and the total extracted to that extracted under laboratory conditions, and (3) evaluate in what stage (early, mid, or late) the municipal leachate is most aggressive in removing inorganic and organic contaminants from the industrial wastes. The work involves the use of two large-scale lysimeters (Fig. B-1, 1.8 m in diameter and 3.6 m in height) containing municipal waste. Volume of municipal waste is approximately 7.5 m^3, weighing approximately 1.5 Mg. The municipal waste was obtained from the City of Oak Ridge, Tennessee, on February 23, 1982, and consisted of a residential waste (collected from households) and a commercial waste (collected from fast-order restaurants, etc.). These wastes are layered in the lysimeter in layers approximately 71 cm thick (Fig. B-1). The bottom of the lysimeter contains pea gravel and silica sand to prevent clogging the outlet with waste. A detailed description of the design is presented in Attachment B. Leachate from each of these lysimeters will be used as influent to individual columns containing each of the four previously studied wastes. There will be four columns for each industrial waste, making a total of 16 columns for each lysimeter (2 experiments x industrial wastes x 2 replications) or a total of 32 industrial waste columns for the total experiment. Blank sand columns will also be used for quality control.

For one-half of the columns, the quantity of waste in each of the columns will correspond to the 95/5 scenario. Leachate quality from these columns, in terms of inorganics and organics, will be compared to laboratory-derived extractions (Section 3.1). The remaining columns will be used to evaluate the stage of aggressiveness of the MWL as a function of the age of the leachate.

3.2.2 Laboratory Comparisons: For each lysimeter, one-half of the columns (4 wastes x 2 replicates) will be used to compare the 95%

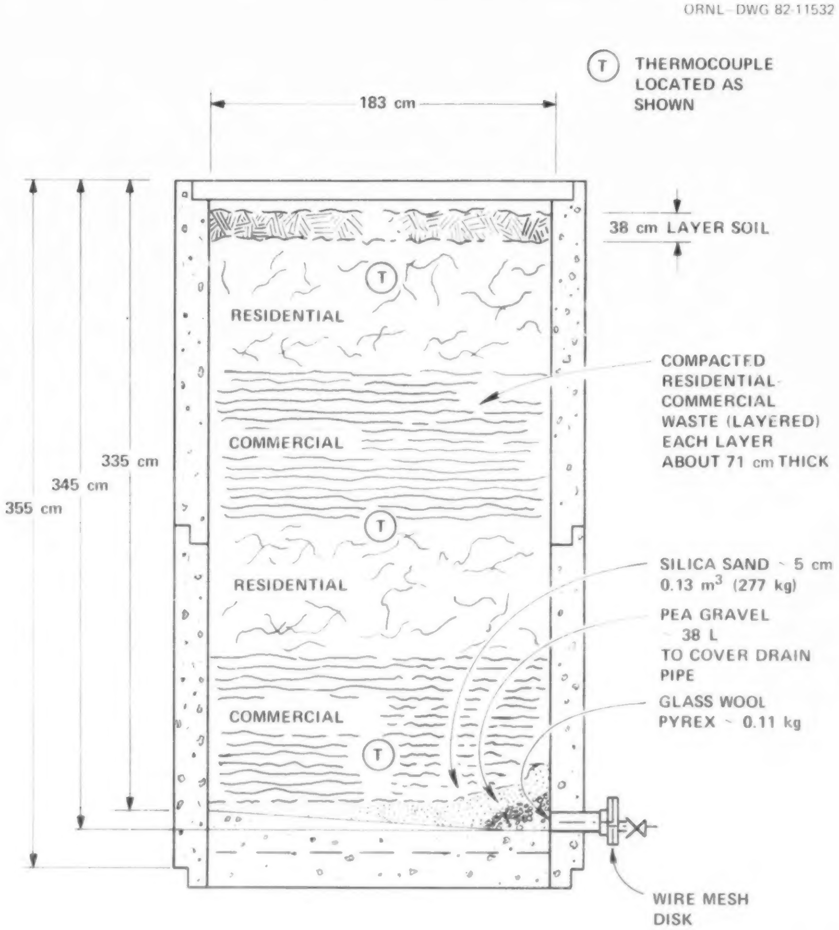
ORNL-DWG 82-11532
T THERMOCOUPLE LOCATED AS SHOWN
183 cm
38 cm LAYER SOIL
RESIDENTIAL
COMMERCIAL
RESIDENTIAL
COMMERCIAL
335 cm
345 cm
355 cm
COMPACTED RESIDENTIAL-COMMERCIAL WASTE (LAYERED) EACH LAYER ABOUT 71 cm THICK
SILICA SAND ~ 5 cm 0.13 m³ (277 kg)
PEA GRAVEL ~ 38 L TO COVER DRAIN PIPE
GLASS WOOL PYREX ~ 0.11 kg
WIRE MESH DISK

Fig. B-1. Schematic of lysimeter containing residential and commerical wastes.

ORNL–DWG 82-11533

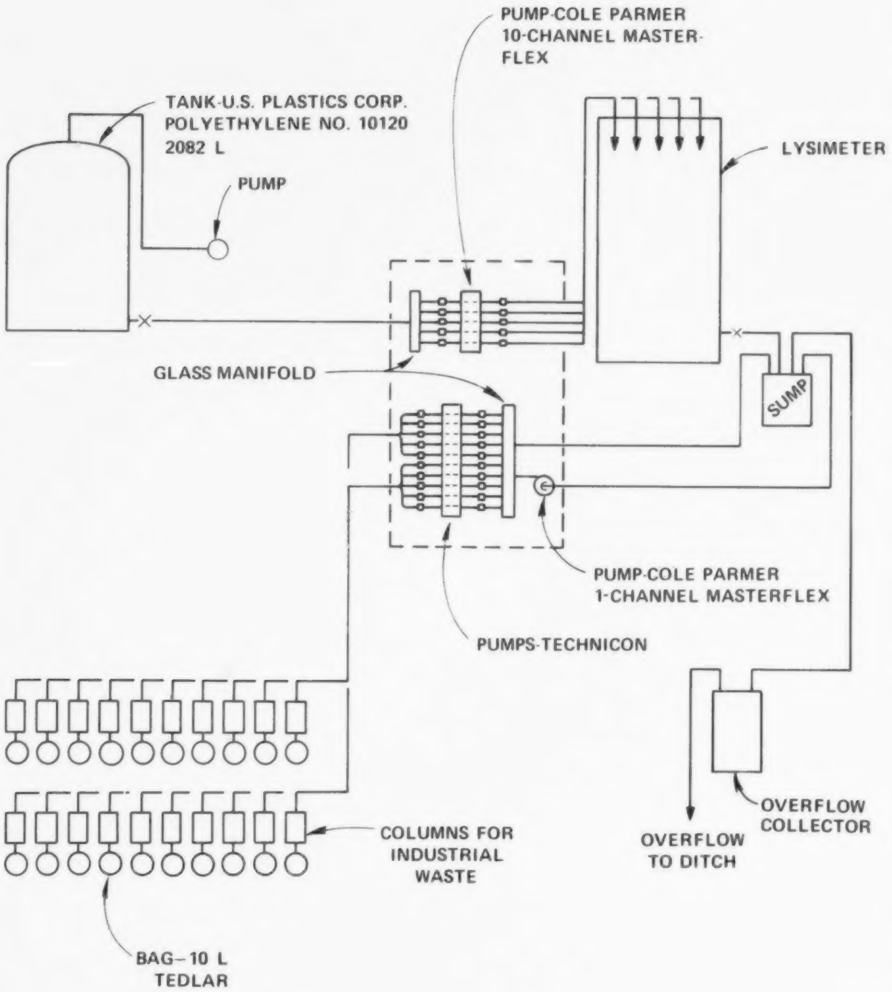
PUMP-COLE PARMER
10-CHANNEL MASTER-FLEX
TANK-U.S. PLASTICS CORP.
POLYETHYLENE NO. 10120
2082 L
PUMP
LYSIMETER
GLASS MANIFOLD
SUMP
PUMP-COLE PARMER
1-CHANNEL MASTERFLEX
PUMPS-TECHNICON
OVERFLOW
COLLECTOR
OVERFLOW
TO DITCH
COLUMNS FOR
INDUSTRIAL
WASTE
BAG–10 L
TEDLAR

Fig. B-2. Flow diagram for lysimeter study.

municipal and 5% industrial waste scenario to the laboratory extraction studies. These columns will contain 3.6 kg of waste and will be leached with the MWL until a 20:1 liquid to solid ratio is achieved (see Section 3.3). At the selected flow rate of 0.8 mL/min (equivalent to a flux of 7 mL m^{-2} min^{-1}) this will require eight weeks (59 d). Samples of leachate will be collected twice weekly the first four weeks and once weekly the remaining four weeks. Aliquots will also be composited to ascertain a concentration of inorganics and organics in the final 20:1 volume.

3.2.3 Aggressiveness of Municipal Waste Leachate over Time: The remaining columns (4 wastes x 2 replications) in the lysimeter design will contain 0.86 kg of waste. Leachate will be collected after 15 d and fresh industrial waste will be substituted in the column. Again the final quantity of leachate collected will correspond to the 20:1 liquid to solid ratio. This portion of the experiment is planned to continue for 90 d (three to four changes of waste). The quantity of inorganic and organic constituents leached from each column of fresh waste should provide an evaluation relative to the aggressiveness of the municipal waste leachate with age of leachate.

3.2.4 Experimental Design and Analysis: The experiment will consist of a randomized block design with four treatments and two blocks (lysimeters). The experiment will be replicated twice to test the block by treatment interaction. An analysis of variance will be conducted to see if there are any differences in leachate aggressiveness due to age of leachate. A multivariate pattern analysis will be used to determine which of the laboratory extraction methods most closely simulates the chemical constituents derived from the field lysimeters. The results from the laboratory and field studies will be combined and statistically analyzed to determine the laboratory method (EP-III) that most closely simulates the mobility of inorganic as well as organic constituents of industrial wastes co-disposed with municipal wastes in a landfill environment.

3.3 Basis of Calculation for Large-scale Lysimeter Research

The large-scale lysimeters (1.8 m in diameter and 3.6 m in height, Fig. B-1) contain approximately 7 m^3 of waste weighing on the order of 1.5 Mg. The wastes were compacted and covered with 0.4 m of soil to simulate a landfill. Distilled water will be continuously added to each lysimeter at a flux of 7 $mL\ m^{-2}\ min^{-1}$ (ca. 26.5 $L\ d^{-1}$ $lysimeter^{-1}$).

Leachate from each lysimeter will be collected in a 27-L sump from which leachate will be pumped to 16 individual industrial waste columns containing the eight industrial wastes replicated two times. Leaching by the municipal waste leachate will be conducted in a downward trickling fashion. The flow rate will be the same as that applied to the surface of the large-scale lysimeters (7 $mL\ m^{-2}\ min^{-1}$). Acid-washed sand will be mixed with the industrial waste (1:1) to increase the hydrologic conductivity. Leaching will continue until a 20:1 liquid: solid ratio is achieved from these columns. Leachate will also be pumped from the sump for special laboratory extraction studies. Any excess leachate will be diverted to ORNL waste treatment facilities. The basis of calculation is as follows:

Area of large-scale lysimeter = 2.54 m^2

Flux = 7 mL min^{-1} m^{-2}

Assume 1.5 Mg of municipal waste/lysimeter, for a 95/5 scenario (78.9 kg of waste is required).

A borosilicate glass column will be used for the industrial wastes [15.2-in. (38.7-cm) i.d., 12 in. (30.5 cm) high, cylindrical jar with a glass outlet being placed on the bottom] will be used. Then the area of each column (0.118 m^2) times 16 (1.88 m^2) represents 74.1% of the area of the lysimeter (1.88/2.54 x 100). Therefore, 74.1% of the leachate from the lysimeter will be required to "feed" the 16 columns containing the industrial wastes. The weight of the industrial wastes in each column will be 3.61 kg (78.9 kg x 0.741 ÷ 16) for the laboratory comparison study and 0.8 kg for the columns used to evaluate the aggressiveness of the MWL with age.

The flow rate to each industrial waste column will be 0.8 mL/min (7 mL min^{-1} m^{-2} x 0.118 m^2). Thus, it will require at this flow rate 59 d to reach a 20:1 solution to solid ratio (72 L) of column leachate for the comparative study.

Total quantity of each industrial waste required will be as follows:

Laboratory studies - 11 x 0.1 kg	= ~23 kg
Field studies - 3.3(4) + 0.8(16)	= ~37 kg
Reserve	= ~40 kg
Total	= ~82 kg

The above calculations and procedures are based on best available information relative to the physical and chemical characteristics of the wastes and anticipated characteristics of the municipal waste leachate. Alterations to these procedures may be necessary to obtain the desired results. For example, mixing the industrial wastes with acid wash sand is intended to (1) increase porosity of the waste/sand mixture so that downflow of the municipal waste leachate can be conducted and (2) decrease the possibility of "hydraulic short circuiting" of the leachate through the relatively thin layer (approximately 2 to 4 cm) of industrial waste. The plan is to mix the wastes with sand on a 1:1 weight basis. Laboratory tests will be conducted prior to installation of the field columns relative to the applicability of the 1:1 mixture to facilitate downward flow of municipal waste leachate. If 1:1 mixture is not a sufficient quantity of sand to sustain flow, a 2:1 sand mixture will be used for that waste. Experiments will also be conducted to evaluate the capacity of the sand to attenuate the mobility of inorganic and organic toxic materials in municipal waste leachate.

4. WORK SCHEDULE

Milestone	Projected Date
1. Laboratory study	
WES municipal leachate procured	Jan. 27, 1982
Industrial wastes (8) procured	May 15, 1982
Proximate analysis of wastes initiated	May 15, 1982
Select wastes (4) for laboratory and field studies	May 31, 1982
Laboratory extractions started (88 extractions)	June 1, 1982
Laboratory extractions completed	Sept. 1, 1982
Inorganic and organic analysis of extracts completed	Sept. 15, 1982
Statistical analyses completed	Oct. 15, 1982
2. Field study	
Municipal refuse obtained and lysimeters packed	Feb. 23, 1982
Industrial waste columns packed for laboratory comparison and aggressiveness of MWL, begin leaching	June 15, 1982
Laboratory comparison, leaching completed	Aug. 10, 1982
Inorganic and organic analyses of leachates from laboratory comparison completed	Sept. 1, 1982
Aggressiveness of MWL, leaching completed	Sept. 15, 1982
Inorganic and organic analyses of leachates from aggressiveness of MWL completed	Oct. 1, 1982
Statistical analyses completed, aggressiveness of MWL	Oct. 15, 1982
3. Draft report on laboratory and field studies	Jan. 1, 1983

TYPIST PROOFER CORRECTOR

5. REFERENCES CITED

Bause, D. E., and K. T. McGregor. 1980. Comparison of four leachate-generation procedures for solid waste characterization in environmental assessment programs. EPA-600/7-80-118. U.S.EPA, Washington, D.C.

Epler, J. L. 1980. Toxicity of Leachates. EPA-600/2-80-057. U.S.EPA, Washington, D.C.

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ATTACHMENT A TO APPENDIX B

PROTOCOL FOR EVALUATING THE AGGRESSIVENESS OF THREE TREATMENT PROCEDURES

1. Rank the concentrations of each constituent extracted from least to most aggressive within each waste.
2. Group the constituents into target analysis categories and then sum the ranks within a category:
   - NIPDWR inorganics
   - Toxic organics.
3. Rank the sums within each category.
4. Sum the ranks across categories to obtain an overall rank sum.
5. Repeat 1-4 for all wastes.
6. Statistically analyze the rank sum.

TYPING PHOTOMASTER - STANDARD 8" SINGLE COLUMN FORMAT
TYPIST PROOFER CORRECTOR

EXAMPLE OF PROTOCOL FOR EVALUATING THE AGGRESSIVENESS OF THREE TREATMENT PROCEDURES FOR A PARTICULAR INDUSTRIAL WASTE

TREATMENTS	TOXIC ORGANICS		NIPDWR INORGANICS		
	Phenol	BAP	Hg	Cd	Pb
1	0.1	0.04	0.5	10	43
2	8.0	0.09	1.6	20	25
3	6.0	0.01	2.0	12	68

STEP 1 - RANK THE CONCENTRATIONS OF EACH CONSTITUENT EXTRACTED

1	1	2	1	1	2
2	3	3	2	3	1
3	2	1	3	2	3

STEP 2 - GROUP THE CONSTITUENTS INTO CATEGORIES AND SUM THE RANKS

TREATMENTS	TOXIC ORGANICS	NIPDWR INORGANICS
1	3	4
2	6	6
3	3	8

STEP 3 - RANK THE SUMS WITHIN EACH CATEGORY

1	1.5	1
2	3	2
3	1.5	3

STEP 4 - SUM THE RANKS ACROSS CATEGORIES TO OBTAIN AN OVERALL RANK SUM

TREATMENT	RANK SUM
1	2.5
2	5
3	4.5

ATTACHMENT B TO APPENDIX B

DESCRIPTION OF LYSIMETER STUDY

A one-line diagram of the lysimeter study setup is depicted in Fig. B-2. A detailed explanation follows. The two large-scale municipal waste lysimeters will be continuously watered using distilled water contained in a 2080-L polyethylene storage tank (U.S. Plastic Corp. Cat. No. 10120). Water out of the storage tank will flow from 0.5-in. (1.3-cm) PVC pipe into a glass manifold that will direct the water into 10 separate master-flex pump channels (Cole Parmer Cat. No. C-7568-00); the pump will be equipped with pump heads and silicone tubing (Cole Parmer head #C-7013-20 and tubing #C-6411-41) to accommodate a flow rate of 3.68 mL min^{-1} channel^{-1}. Five channels will continuously provide water to each lysimeter at 3.68 mL/min (a total of 18.4 mL/min or 26.5 L/d). Each lysimeter will be covered with a 0.015-cm thick polyethylene tarp.

Municipal waste leachate (MWL) out of each lysimeter will be delivered to separate 27-L glass sumps (30.5 cm o.d. x 45.7 cm high, Corning No. 6942) through 2.54-cm PVC pipe. A 2.0-cm-thick plexiglass cover with the underside covered with Teflon® overlay (with holes cut for inlets and outlets) will be fabricated to fit each sump jar. An overflow pipe will be connected to the sumps to divert any excess MWL to ORNL waste treatment facilities; a sampling port will be connected to the overflow pipe to collect MWL for characterization and/or laboratory studies. MWL for industrial waste leaching will be pumped from the sump (30 mL/min) to a glass manifold using a masterflex pump (Cole Parmer pump no. 7545-10, pumphead no. C-7016-00); excess MWL not

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used for industrial waste leaching will return to the sump. The MWL will contact Teflon® tubing except through the pump which utilizes silicone tubing [0.125-in. (0.32-cm) i.d., 0.251-in. (0.64-cm) o.d., Cole Parmer Cat. No. C-641102]. The glass manifold will contain inputs to monitor the pH and Eh of the MWL and will also be fitted with 22 ports (Note: All may not be used) to aliquot the MWL to the industrial waste columns. Each industrial waste column (16 per lysimeter plus 2 sand controls) will receive MWL at a flow rate of 0.8 mL/min. The MWL will be pumped, using Technicon pumps (2-speed proportioning pump) from each manifold port (each channel in the pump will connect to a port in the manifold) through 0.125-in. (0.32-cm) o.d. Teflon® tubing connected to Technicon solvent flexible manifold tubing [0.045-in. (0.11-cm) i.d. Technicon No. 1160533]; 0.125-in. (0.32-cm) o.d. Teflon® tubing will be connected out of the pump and will introduce the MWL to the industrial waste columns. The industrial waste columns are purchased borosilocate glass jars (32-L capacity, 38.7-cm i.d. and 30.5 cm high, Corning No. 6942) with an outlet placed on the jar bottom. A 2.0-cm-thick plexiglass cover with the underside covered with Teflon® overlay will be fabricated to seal the jar top. Leachate out of the industrial columns will flow through Teflon® tubing into Tedlar sampling bags.

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